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## PHASE TRANSITIONS IN FERROELECTRICS

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## PHASE TRANSITIONS OF DISPLACEMENT TYPE IN FERROELECTRICS

V. G. Vaks

*ABSTRACT: The statistics and dynamics of displacement type phase transitions in ferroelectrics are described in microscopic terms. The coefficients of the Devonshire expansion of the free energy are expressed through the microscopic parameters. The correlation effects in the transition region are examined. The spectrum of the low-frequency vibrations above and below the transition point is found.*

## 1. INTRODUCTION

The phase transitions in ferroelectrics are usually divided into two classes as being of order-disorder type or of displacement type [2]. In the order-disorder transitions (for example, in  $\text{KH}_2\text{PO}_4$  or triglycine sulfate), the ions or radicals that determine the polarization of the crystal have a number (usually two) of symmetric sites of equilibrium in the cell. Since the sites are at a substantial distance from one another, the total potential in which the ion moves is markedly anharmonic. Above the Curie point  $T_c$  the sites have a statistically uniform population, but below  $T_c$  there is spontaneous asymmetry of the population leading to a polarization. The character of the phase transition under those conditions is identical to the familiar Ising model [2], and, in particular, the transition is usually of the second kind. The theoretical description of the order-disorder transitions comes up against the usual difficulties of allowance for the strong correlations in phase transitions of the second kind, whereas the present case requires allowance for the effect of long-range forces of dipole-dipole interaction as well [3]. However, the dynamical effects involved in the possibility of non-relaxational vibrations of the ions between equilibrium sites are usually exponentially small [4], and the high-frequency dynamics of the crystal has no singularities close to  $T_c$  [4,5].

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The displacement-type transitions pertaining to ferroelectrics of octahedral oxide type [1] (for example,  $\text{BaTiO}_3$ ) are characterized by the fact that the anharmonicity of the potential for all

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\*Numbers in the margin indicate pagination in the foreign text.

the ions has the small order of magnitude that is usual for crystals. At ordinary temperatures  $T$  that are small as compared with the atomic energies  $\epsilon_{at}$ , the phase transition is due to a special contraction (typical of these structures) of the components that determine hardness with respect to a given strain on the cell [6,7]. The small magnitude of the anharmonicity permits the transition to be described by the usual methods of expansion in powers of the ratio of vibrational amplitudes to the dimensions of the cell, i.e.,  $T/\epsilon_{at}$ . In that connection, as will be shown below, the correlational effects characteristic of phase transitions of the second kind are also proportional to  $T/\epsilon_{at}$  and are everywhere small except for temperatures extremely close to the point of the transition of the second kind,  $T_c$ . On the other hand, since a transition of the first kind usually occurs in displacement-type transitions before  $T_c$  is reached, there is no danger zone and the expansion in powers of this anharmonicity can be applied for all  $T$ 's. In thermodynamics this implies a Devonshire expansion in powers of the polarization [8], and in dynamics it corresponds to the attainment of a critical vibration called the Cochran vibration with a small and very temperature-dependent gap in the energy spectrum [7,9-12,4]. /6

The foregoing considerations, which have been developed in papers by a number of authors [6-13], make it possible to formulate a quantitative theory of displacement-type transitions on the basis of microscopic conceptions. Since the anharmonic components play a decisive part in the transition, in the present case there is a rare opportunity for direct determination of the microscopic parameters of the anharmonicity through macroscopic quantities. Concurrently, the same constants determine both the thermodynamics and the dynamics of the system in the region of small wave-vectors  $\vec{k}$  which has an important bearing on critical effects near the transition. Therefore, the microscopic approach should permit one to relate the thermodynamic properties with such dynamic characteristics as the temperature dependence of the frequency and width of the critical vibration, the dielectric losses at high and microwave frequencies, and the probability of the Mössbauer effect in the vicinity of the transition.

A microscopical approach to the thermodynamics of displacement type ferroelectrics was developed in the work of Kwok and Miller [8] who obtained an expression for the phenomenological parameters of the Devonshire expansion in terms of microscopic quantities. However, a few questions were not examined in [8], including in particular the thermodynamic contribution of the critical degrees of freedom and the correlation effects. Moreover, the microscopic expressions given there omit a number of terms which have, generally speaking, the same order of magnitude as the terms included. Therefore, in Sections 3 and 4 the microscopical expression for the Devonshire coefficients will be improved and correlational effects will be discussed. The fundamental purpose of the work is to /7

examine the dynamics in the transitional region. In Section 5, the general expression for the phonon Green's function will be used to obtain equations for the vibrational spectrum of the system in the region of small  $\vec{k}$  with allowance for the coupling of the acoustical and optical degrees of freedom and the piezoelectric effect. Thus, a microscopical derivation is given for the semiphenomenological equations of Ginzburg [9,14] and Cochran [10,11], and their generalization is given for the case of non-zero  $\vec{k}$  and the region below the transition. From those equations, an expression will be found for the spectrum of the critical vibrations. A marked and mutual influence is noted between the critical and acoustical branches. It is found that the spectrum of the five low-lying branches for small  $\vec{k}$  in the perovskites is determined by six constants; hence, an experimental study of that spectrum will permit determination of those important characteristics of the crystal. The temperature dependence of the squared displacements of the ions and the Mössbauer effect close to the transitions will be examined in another paper.

The examination will refer to an ideal single-domain crystal. Specifically, the case to be discussed is that of the perovskites, but the extension to other cases is obvious. A temperature-diagram technique [15] will be employed as being the most concise method for simultaneous description of statistical and dynamical properties. The method and the qualitative findings, including the existence of the critical vibration, can be applied to the case of non-ferroelectric displacement-type transitions as well [9,4].

## 2. THE HAMILTONIAN AND THE DIAGRAM TECHNIQUE

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As usual, we shall examine the crystal in the adiabatic approximation, assuming that the energy of the system is completely defined by the statement of the coordinates and velocities of the centers of the ions. Then, if we expand the potential energy in the usual manner in powers of the deviations of the ions from the equilibrium sites in the cubic phase [7,8], for the Hamiltonian we shall have

$$\begin{aligned}
 H = & \frac{1}{2} \sum_{\vec{r}} m_i \left( \dot{\vec{u}}_{\vec{r}}^i \right)^2 + \frac{1}{2} \sum_{\substack{i_1 i_2 \\ \vec{r}_1 \vec{r}_2}} \phi_{\alpha_1 i_1 \alpha_2 i_2}(\vec{r}_1 - \vec{r}_2) u_{\vec{r}_1}^{\alpha_1 i_1} u_{\vec{r}_2}^{\alpha_2 i_2} - \sum_{\vec{r}} e_i \dot{\vec{u}}_{\vec{r}}^i \vec{E} + \\
 & \frac{1}{8\pi} \int \left( \vec{E}^2 + \vec{H}^2 \right) dV + \sum_{n=3}^{\infty} \frac{1}{n!} \phi_{\alpha_1 i_1 \dots \alpha_n i_n}(\vec{r}_1, \dots, \vec{r}_n) u_{\vec{r}_1}^{\alpha_1 i_1} \dots u_{\vec{r}_n}^{\alpha_n i_n}. \quad (1)
 \end{aligned}$$

Here  $\vec{u}_{\vec{r}}^i$  and  $\dot{\vec{u}}_{\vec{r}}^i$ , respectively, are the displacement and the velocity

operators of the  $i$ -th ion in a cell that is characterizable by the lattice vector  $\vec{r} = n_1 \vec{a}_1 + n_2 \vec{a}_2 + n_3 \vec{a}_3$ ; the  $\vec{a}_i$ 's are the fundamental periods, which in the present case form a Cartesian trihedral of vectors. The  $\phi$ 's are the coefficients in the expansion of the potential energy. The interaction  $\phi_{(\vec{r}_1 - \vec{r}_1)}^{\alpha_1 i_1 \alpha_2 i_2}$  includes only the short-range forces, particularly the difference between the field acting on the ion and the average field, but does not include the components corresponding to the long-range Van der Waals forces. The latter effects are described with the average macroscopic field  $E$  which can be regarded as an independent dynamic variable;  $e_i$  is the effective charge of the ion, while the neutrality of the cell implies  $\sum_i e_i = 0$ . The coefficients  $\phi$  satisfy certain relations that follow from the invariance of the energy of the crystal in homogeneous displacement:

$$\begin{aligned}
 u_{\vec{r}}^{\alpha i} &\rightarrow u_{\vec{r}}^{\alpha i} + \text{const:} \\
 \sum_{i_1 \vec{r}} \phi_{(\vec{r})}^{\alpha_1 i_1 \alpha_2 i_2} &= \sum_{i_2 \vec{r}} \phi_{(\vec{r})}^{\alpha_1 i_1 \alpha_2 i_2} = 0; \\
 \sum_{i_m \vec{r}_m} \phi_{(\vec{r}_1, \dots, \vec{r}_m, \dots, \vec{r}_n)}^{\alpha_1 i_1 \dots \alpha_m i_m \dots \alpha_n i_n} &= 0.
 \end{aligned} \tag{2}$$

After the usual conversion to Fourier components,

$$\begin{aligned}
 u_{\vec{k}}^i &= \frac{1}{\sqrt{N}} \sum_{\vec{r}} u_{\vec{r}}^i e^{-i\vec{k}\vec{r}}; \quad \phi_{(\vec{k})}^{\alpha_1 i_1 \alpha_2 i_2} = \sum_{\vec{r}} \phi_{(\vec{r})}^{\alpha_1 i_1 \alpha_2 i_2} e^{-i\vec{k}\vec{r}}; \\
 \vec{E}_{\vec{k}} &= \frac{1}{\sqrt{N}} \sum_{\vec{r}} \vec{E}_{\vec{r}} e^{-i\vec{k}\vec{r}}
 \end{aligned} \tag{3}$$

where  $\vec{u}_{\vec{k}}$  is the quasi-momentum and  $N$  the number of cells, the Hamiltonian (1) assumes the form

$$H = H_0 + H_{int} = \frac{1}{2} \sum_{\vec{k}} \left[ \sum_i \left( m_i \dot{u}_{\vec{k}}^i \dot{u}_{-\vec{k}}^i - 2e_i \dot{u}_{\vec{k}}^i \vec{E}_{-\vec{k}} \right) + \sum_{ij} \phi_{(\vec{k})}^{\alpha i \beta j} u_{\vec{k}}^{\alpha i} u_{\vec{k}}^{\beta j} + \right.$$

$$\left. \frac{v_c}{4\pi} \left( \vec{E}_{\vec{k}} \vec{E}_{-\vec{k}} + \vec{H}_{\vec{k}} \vec{H}_{-\vec{k}} \right) \right] + H_{int} . \quad (4)$$

Here  $v_c$  is the volume of the unit cell and  $H_{int}$  stands for the last component of (1), expressed through  $\vec{u}_{\vec{k}}^i$ . In the present paper we shall not be concerned with the short-wave electromagnetic radiation of wavelengths less than or of the order of the dimension of the cell (x-ray region); hence, we can confine ourselves to expressing the dynamic variables for the field through its values at the lattice sites. In that connection, the summands of  $\vec{E}_{\vec{k}}$  in (3) are defined in the same way as  $\vec{u}_{\vec{k}}^i$  while the factor  $v_c$  appears in the next to the last term of (4).

The quadratic expression in parentheses in (4) usually can be reduced to a diagonal form corresponding to non-interacting phonons [8]. However, if we have in mind an application to the study of spectra with small  $\vec{k}$  and of the displacements of the individual ions, it is more convenient to carry out a transformation as follows: As the "acoustical" variable we select the coordinate  $\vec{u}_{\vec{k}}^1 \equiv \vec{u}_{\vec{k}}$  of the given ion, and in place of the remaining  $\vec{u}_{\vec{k}}^i$  we introduce the relative coordinates  $\vec{y}^i = \vec{u}_{\vec{k}}^i - \vec{u}_{\vec{k}}$ . Furthermore, we carry out a canonical transformation of the "optical" variables  $\vec{y}_{\vec{k}}^i$  with coefficients independent of  $\vec{k}$  such that for  $k = 0$  the summands quadratic with respect to  $\vec{y}$  and  $\dot{\vec{y}}$  in the Hamiltonian  $H_0$  in (4) will assume a diagonal form:

$$y_{\vec{k}}^{i\alpha} = \frac{1}{\sqrt{m_i}} \sum_j e_j^{i\alpha} x_{\vec{k}}^j ; \quad \sum_i m_i (\dot{y}_0^i)^2 + \sum_{i,l} \Phi_{(0)}^{i\alpha l \beta} y_0^{i\alpha} y_0^{l\beta} = \sum_j \left( \dot{x}_{j0}^2 + \lambda_j x_{j0}^2 \right). \quad (5)$$

In the present case of perovskites with five ions in the cell, the quantities  $j$  in (5) pass through 12 values. As noted by Kwok and Miller [8], owing to the cubic symmetry, the 12 quantities  $\lambda_j$  in (5) break up into four thrice degenerate values  $\lambda_b$  ( $b = 1, 2, 3, 4$ ), and for each  $b$  three unit vectors  $\vec{e}_j = \vec{e}_{b\sigma}$  correspond to three polarizations  $\sigma$  along the principal axes of the crystal:

$$e_{b\sigma}^{i\alpha} = \sqrt{m_i} v_i(b) \delta_{\alpha\sigma}; \quad \vec{y}_{\vec{k}}^i = \sum_b v_i(b) \vec{x}_{b\vec{k}}^i; \quad \left( \vec{x}_{b\vec{k}}^i \right)_\sigma = x_{\vec{k}}^{b\sigma}. \quad (6)$$

After the transformations carried out above, the Hamiltonian (4) assumes the form

$$\begin{aligned}
H_0 + H_{int} = \frac{1}{2} \sum_{\vec{k}} \left[ M \vec{u}_{\vec{k}} \cdot \vec{u}_{-\vec{k}} + \vec{u}_{\vec{k}} A \vec{u}_{-\vec{k}} + \frac{v_c}{4\pi} \left( \vec{E}_{\vec{k}} \cdot \vec{E}_{-\vec{k}} + \vec{H}_{\vec{k}} \cdot \vec{H}_{-\vec{k}} \right) + \right. \\
\sum_b \left( 2 \vec{u}_{-\vec{k}} \sqrt{\mu_b} \cdot \vec{x}_{b\vec{k}} + 2 \vec{u}_{-\vec{k}} V_b \vec{x}_{b\vec{k}} - 2 z_b \vec{E}_{-\vec{k}} \cdot \vec{x}_{b\vec{k}} + \right. \\
\left. \left. \vec{x}_{b\vec{k}} \cdot \vec{x}_{b-\vec{k}} + \lambda_b \vec{x}_{b\vec{k}} \cdot \vec{x}_{b-\vec{k}} \right) + \left. \left. \vec{x}_{b\vec{k}} \cdot \vec{x}_{b'b-\vec{k}} S_{bb'} \vec{x}_{b'-\vec{k}} \right) \right] + H_{int}. \quad (7)
\end{aligned}$$

Here we have introduced the notation

$$\begin{aligned}
M = \sum_i m_i; \quad \sqrt{\mu_b} = \sum_i m_i v_i(b); \quad z_b = \sum_i e_i v_i(b); \quad A_{(\vec{k})}^{\alpha\beta} = \sum_{ij} \Phi_{(\vec{k})}^{i\alpha j\beta}; \\
V_{b(\vec{k})}^{\alpha\beta} = \sum_{ij} \Phi_{(\vec{k})}^{i\alpha j\beta} v_j(b); \quad S_{bb',(\vec{k})}^{\alpha\beta} = \sum_{ij} v_i(b) \Phi_{(\vec{k})}^{i\alpha j\beta} v_j(b') - \lambda_b \delta_{bb'} \delta_{\alpha\beta}; \quad (8)
\end{aligned}$$

and in the Hamiltonian  $H_{int}$  the displacements  $\vec{u}^i$  are expressed through  $\vec{u}, \vec{x}_b$ .

The matrices  $A$ ,  $V$ , and  $S$  in (7) and (8) go to zero at small  $\vec{k}$ . That is implied for  $A$  and  $V$  by (2) and (3) and for  $S$  by (5) and (6). Owing to the splitting-off of the long-range electromagnetic forces into a separate term, the potentials  $\Phi(\vec{k})$  and the matrices  $A$ ,  $V$ , and  $S$  are analytic on small  $\vec{k}$ . Hence, for  $k$  smaller than the reciprocal dimension  $1/a$  of the cell, and with allowance for cubic and mirror symmetry, the expansion of these matrices can be written in the form

$$\begin{aligned}
\hat{A} = Mk^2 \left( a_l g^l + a_t g^t + a_a g^a \right); \quad \hat{V} = k^2 \sqrt{M} \left( v_l g^l + v_t g^t + v_a g^a \right); \\
S = k^2 \left( s_l g^l + s_t g^t + s_a g^a \right). \quad (9)
\end{aligned}$$

Here, by way of abbreviation, the indices  $b$  and  $b'$  have been omitted from the matrices  $V$  and  $S$ ;  $a_i$ ,  $v_i$  and  $s_i$  are constants; and the



tensors  $g^i$  depend only on the angles of the vector  $\vec{n} = \vec{k}/k$ :

$$g_{\alpha\beta}^l = n_\alpha n_\beta; \quad g_{\alpha\beta}^t = \delta_{\alpha\beta} - n_\alpha n_\beta; \quad g_{\alpha\beta}^a = \sum_{\sigma=1}^3 e_\sigma^\alpha e_\sigma^\beta (\vec{n} \vec{e}_\sigma)^2, \quad (10)$$

where  $\vec{e}_\sigma$  is the unit vector of the principal axis  $\sigma$ . In formulas (9) for  $A$  and  $V$ , the mass  $M$  of the cell has been split off as a multiplier to reduce the quantities  $a_i$ ,  $v_i$  and  $s_i$  to a single dimension, the square of the velocity. At the same time, the constants  $a_i$  are expressed through the elastic moduli  $C_{ik}$  as follows:

$$a_l = \left( c_{11} + \frac{c_{44}}{2} \right) \frac{1}{\rho}; \quad a_t = \frac{c_{44}}{4\rho}; \quad a_a = \left( c_{11} - c_{12} - \frac{c_{44}}{2} \right) \frac{1}{\rho}, \quad (11)$$

where  $\rho = \mu/v_c$  is the density. The quantities with the index "a" in (9) define the degree of crystalline anisotropy; for example,  $a_a$  defines the elastic anisotropy of the crystal.

As has been noted by a number of authors [7,8] and as will be evident in what follows, the phase transition takes place at temperatures  $T$  much lower than the atomic energies  $\epsilon_{at}$  if and only if one of the constants  $\lambda_b$  in (5) and (7) which we shall call  $\lambda_c$  is negative and small as compared with the other  $\lambda_r$ , being a quantity of the order of  $\lambda_r T/\epsilon_{at}$ . We shall call the corresponding degree of freedom the critical degree of freedom  $\vec{x}_c$ ; we shall designate the other "b"'s by the letter  $r$ . Owing to the smallness of  $\lambda_c$  for the critical degree of freedom at small  $\vec{k}$ , substantial magnitudes are assumed by the anharmonic contributions arising from  $H_{int}$  as well as by the terms from  $V_c$  and  $S_{cc}$  that are proportional to  $k$ . For the other degrees of freedom, the analogous corrections are negligible as compared with the large quantities  $\lambda_r$ . /11

Let us choose a normal calibration of the potentials of the electromagnetic fields:  $\text{div } \vec{A} = 0$ ,  $\vec{A} = \vec{A}_t$ . Then the dynamic variables in the Hamiltonian (7) will be the coordinates  $\vec{u}$  and  $\vec{x}_b$ , the scalar potential  $\phi$ , and  $\vec{A}_t$ . Therefore, if we introduce the eighteen-component vector  $\xi_i$  with components  $(\vec{u}, \vec{x}_b, \phi, \vec{A}_t)$  we will be able to write the temperature Green's function of the system [15] in matrix form:

$$G_{ij}(\vec{k}, i\omega_n) = \int_0^\beta d\tau e^{i\omega_n \tau} \sum_{\vec{r}_2} e^{i\vec{k}(\vec{r}_2 - \vec{r}_1)} \langle \hat{T}(\xi_i(\vec{r}_1, 0) - \bar{\xi}_i) (\xi_j(\vec{r}_2, \tau) - \bar{\xi}_j) \rangle. \quad (12)$$

The symbols here are:  $\beta = 1/T$ ;  $\hat{T}$  is the sign of  $T$ -ordering [15];  $i\omega_n = 2i\pi nT$  are the imaginary frequencies of the temperature diagram technique;  $\xi_i(\tau) = e^{H\tau} \xi_i e^{-H\tau}$ ,  $\bar{\xi}_i = \langle \xi_i \rangle$ , and the mean of the expressions in brackets stands for the trace

$$\langle \dots \rangle = S_p[(\dots) \exp(-\beta H)] \cdot [Sp \exp(-\beta H)]^{-1}$$

The zero Green's function  $G_0$  corresponds to the Hamiltonian  $H_0$  in (7) and as usual is defined by the equation [15]

$$H^0_{ij} G^0_{jl} = \delta_{il}$$

where  $H^0_{ij}$  stands for the coefficients of  $\frac{1}{2} \xi_i \xi_j$  in (7) with the operator replaced by the derivative of the imaginary frequency with the time ( $\frac{d}{dt} \rightarrow \omega_n$ ) and with a change of sign in the diagonal term corresponding to the scalar potential [15] ( $H^0_{\phi\phi} = -\frac{k^2 v_c}{4\pi}$ ). The explicit expression of the matrix  $G_0^{-1}$  has the form:

$$G_0^{-1}(k, i\omega_n) = \begin{pmatrix} M\omega_n^2 + A & \omega_n^2 \sqrt{\mu_b} + V_b & 0 & 0 \\ \omega_n^2 \sqrt{\mu_b} + V_b^+ & \omega_n^2 + \lambda_b + S_{bb} & i\vec{k}z_b & z_b \frac{\omega_n}{c} \\ 0 & -i\vec{k}z_b & -\frac{k^2 v_c}{4\pi} & 0 \\ 0 & -z_b \frac{\omega_n}{c} & 0 & \frac{v_c}{4\pi} \left( \frac{\omega_n^2}{c^2} + k^2 \right) \end{pmatrix} \quad (13)$$

Here the first line and column correspond to displacements  $\vec{u}$ , the second to  $\vec{x}_b$ , the third to  $\phi$ , and the fourth to  $\vec{A}_t$ ;  $V^+$  stands for the matrix that is the Hermitian conjugate of  $V$ . It is assumed that

the wave vector  $k$  is much greater than the reciprocal dimensions  $1/L$  of the specimen; otherwise,  $\vec{k}$  must be taken as an operator of differentiation with respect to the coordinate (see Section 5).

The anharmonic term in (7) can be written as

$$H_{int} = \sum_{n=3}^{\infty} \frac{1}{n!} \sum_{i_1, i_2, \dots, i_n} \xi_{i_1} \xi_{i_2} \dots \xi_{i_n} V_{i_1 i_2 \dots i_n}^{(n)} \quad (14)$$

Each of the displacements  $\xi_i$  entering into (14) is understood to have the momentum index  $\vec{k}_i$ , while the potentials  $V_{i_1 \dots i_n}^{(n)} = V_{\vec{k}_1 \dots \vec{k}_n}^{(n)}$  are nonzero only for values of the total momentum equal to the vector  $\vec{b}$  of the reciprocal lattice:  $\vec{k}_1 + \vec{k}_2 + \dots + \vec{k}_n = \vec{b}$ .

The diagrammatic technique is formulated in the usual manner [13,15]. Each Green's function (11) is represented on the graph as a solid line, and each term  $V^{(n)}$  in (14) is represented as a vertex with  $n$  outgoing lines. As in the case of a non-ideal Bose gas [15, 8], moreover, one must isolate the nonzero mean values of the coordinates  $\vec{x}_b$  and the deformations  $u_{a\beta}$  in the optical and acoustic degrees of freedom, respectively. Diagrammatically, the means will be pictured as small crosses with dotted lines going out from them. After computation of the free energy  $F$ , the equilibrium values of the homogeneous displacements and deformations can be found from the condition of minimum  $F$ .

### 3. COMPUTATION OF THE FREE ENERGY

Taking into account what has been said in Section 2, we can write the graphic expression for the densities of the free energy  $F$  in the form

$$F = \text{[diagrams a through l]} \quad (15)$$

In estimating the order of magnitude of the different terms of (15), let us assume as a specific example that the phase transition occurs at temperatures greater than the Debye point of the crystal  $\theta_D$ , as in most of the perovskites and in  $\text{BaTiO}_3$ . We also take into account the fact that the deformations  $u_{\alpha\beta}$  and the square of the spontaneous polarization  $P^2$  in atomic units have the order of  $T$ , while the anomalous rigidity  $\lambda_c \sim \lambda_r T / \epsilon_{at}$ . Then the first six terms  $l_a^{-1} l_f$  in expansion (15) have the order of  $T^2$ , and the other terms, that of  $T^3$ . These latter terms could be neglected in the case of "normal" transition of the second kind, in which the temperature-invariant constants in  $l_a^{-1} l_f$  and  $l_g^{-1} l_l$  have one and the same atomic order of magnitude. However, the fact that the transition is a transition of the first kind close to the second kind, and the fact that the coefficient  $B$  in the fourth power of the polarization in the Devonshire expansion is highly dependent on the temperature [1], indicate an anomalously small magnitude of  $B$  with respect to the constants of the following approximation and also indicate that corrections to  $B$  must be included. The temperature contributions to the other quantities, such as the coefficients of elasticity or electrostriction, are already negligible [1]. That has been taken into account in the plotting of the diagram in Figure 1, where the circles with three outgoing dotted lines, for example, are omitted, since hardly one of these dotted lines should correspond to an acoustic deformation on considerations of parity [8].

With (7) and (14), the analytic expression corresponding to (15) is written in the form:

$$\begin{aligned}
 F - F_0(T) = & \frac{1}{2} c_{\alpha\beta\gamma\delta} u_{\alpha\beta} u_{\gamma\delta} + \frac{1}{v_c} \sum_b \left( \lambda_b \frac{\vec{x}_b^2}{2} - z_b \vec{x}_b \vec{E} \right) + \frac{-2}{8\pi} + \\
 & \xi_i \frac{\gamma_i T}{2v_c} + \bar{\xi}_i \bar{\xi}_j \frac{T d_{ij}}{4v_c} + \frac{\bar{\xi}_i \bar{\xi}_j \bar{\xi}_l}{v_c 3!} V_{ijl}^{000} + \frac{\bar{\xi}_i \bar{\xi}_j \bar{\xi}_l \bar{\xi}_m}{v_c 4!} \left( V_{ijlm}^{0000} + \frac{T e_{ijlm}}{2} \right) + \\
 & \frac{\bar{\xi}_{i_1} \bar{\xi}_{i_2} \dots \bar{\xi}_{i_6}}{v_c 6!} V_{i_1 i_2 \dots i_6}^{00\dots 0} .
 \end{aligned} \tag{16}$$

Here,  $F_0(T)$  stands for the path of the free energy that does not depend on the mean displacement, and we have:

$$\gamma_i = \sum_{\vec{k}n} V_i^0 \vec{k} - \vec{k} \vec{i}_1 \vec{i}_2 G_{i_1 i_2}^{\vec{k} n} ;$$

$$d_{ij} = \sum_{\vec{k}n} \left( V_{iji_1i_2}^{00\vec{k}-\vec{k}} G_{i_1i_2}^{\vec{k}n} - V_{i i_1i_2}^{0\vec{k}-\vec{k}} \left| V_{j i_3i_4}^{0\vec{k}-\vec{k}} G_{i_2i_3}^{\vec{k}n} G_{i_4i_1}^{\vec{k}n} \right| \right);$$

$$e_{ijlm} = \sum_{\vec{k}n} \left[ V_{ijlmi_1i_2}^{0000\vec{k}-\vec{k}} G_{i_1i_2}^{\vec{k}n} - \left( 3V_{iji_1i_2}^{00\vec{k}-\vec{k}} V_{lmi_3i_4}^{00\vec{k}-\vec{k}} + 2V_{ijli_1i_2}^{000\vec{k}-\vec{k}} V_{mi_3i_4}^{0\vec{k}-\vec{k}} \right) \right.$$

$$G_{i_2i_3}^{\vec{k}n} G_{i_4i_1}^{\vec{k}n} + GV_{iji_1i_2}^{00\vec{k}-\vec{k}} V_{li_3i_4}^{0\vec{k}-\vec{k}} V_{mi_5i_6}^{0\vec{k}-\vec{k}} G_{i_2i_3}^{\vec{k}n} G_{i_4i_5}^{\vec{k}n} G_{i_6i_1}^{\vec{k}n} -$$

$$\left. V_{i i_1i_2}^{0\vec{k}-\vec{k}} V_{j i_3i_4}^{0\vec{k}-\vec{k}} V_{li_5i_6}^{0\vec{k}-\vec{k}} V_{mi_7i_8}^{0\vec{k}-\vec{k}} G_{i_2i_3}^{\vec{k}n} G_{i_4i_5}^{\vec{k}n} G_{i_6i_7}^{\vec{k}n} G_{i_8i_1}^{\vec{k}n} \right]. \quad (17)$$

The upper indices of the potential  $V$  stand for the values of the momenta;  $G^{\vec{k}n} = G(\vec{k}i\omega_n)$ . The repeated Greek letter indices are understood to mean summation from one to three and the English indices are understood to mean summation over all coordinates from one to 15. The symbol  $\bar{\xi}_i$  for optical coordinates  $\vec{x}_b$  stands for a simple mean  $\bar{\vec{x}}_b$ , while for acoustical coordinates it stands for deformation  $u_{\alpha\beta}$ . In the latter case, the index "0" in the potential  $V_{\alpha\ldots}^{0\ldots}$  actually stands for the limit for  $k \rightarrow 0$  of the corresponding derivative of this potential multiplied by  $(-i)$  [8]:

$$\lim_{k \rightarrow 0} \left( u_{\vec{k}}^{\alpha} V_{\alpha\ldots}^{\vec{k}\ldots} \right) = \frac{1}{2} \left( u_{\vec{k}}^{\alpha} k^{\beta} + u_{\vec{k}}^{\beta} k^{\alpha} \right) \frac{\partial}{\partial k_{\beta}} V_{\alpha\ldots}^{\vec{k}\ldots} \Big|_{\vec{k}=0} =$$

$$u_{\alpha\beta} \left( -i \frac{\partial}{\partial k_{\beta}} V_{\alpha\ldots}^{\vec{k}\ldots} \right) \Big|_{\vec{k}=0}, \quad (18)$$

since the potential  $V_{\alpha\ldots}^{0\ldots}$  itself is equal to zero owing to (2).

For what follows, it is important [7] that in the integrals over  $\vec{k}$  in (17) the region of large-wave vectors  $k \sim 1/a$  is substantial since the contribution of the region of small  $k$  is suppressed by the statistical weight of  $\sim k^3$ . For those fairly large  $\vec{k}$ , in the Green's function the influence of  $\lambda_c$  and of the temperature-dependent anharmonic corrections, remains small even for the criti-

cal branch since the coefficients  $s_i$  (9) have, generally speaking, the normal atomic order of magnitude. Therefore, in the first approximation the functions  $G$  in (17) can be replaced by  $G^{00}(\vec{k}, i\omega_n)$  as given by (13) for  $\lambda_c = 0$ . The influence of the subsequent terms is discussed in Section 4. After the substitution, the quantities  $\gamma_i$ ,  $d_{ij}$ ,  $e_{ijlm}$  in (17) are smooth functions of temperature and for  $T > \theta_D$ , in which case we can confine ourselves to the classical summand with  $n = 0$  in the sums over  $n$  in (17). Those quantities are constant.

To state  $F$  in terms of polarization and strain, we also take into account [8] that the zero potential displacement of the critical coordinate average  $\overline{\vec{x}_c}$  is much greater than the residual displacement averages  $\overline{\vec{x}_r}$  since in the determination of  $\overline{\vec{x}_b}$  from the condition  $\partial F / \partial \overline{\vec{x}_b} = 0$  the displacements of  $\overline{\vec{x}_r}$  are inversely proportional to the normal hardnesses  $\lambda_r$  while  $\overline{\vec{x}_c}$  are inversely proportional to the sum of  $\lambda_c$  and of the anharmonic corrections of the order of  $\sim \lambda_r T / \epsilon_{at}$ . Correspondingly, the polarization  $\vec{\Phi}$  of the unit volume is determined by the coordinate  $\overline{\vec{x}_c}$ :

$$\vec{P} = \frac{1}{v_c} \sum_b z_b \overline{\vec{x}_b} \approx \frac{z_c \overline{\vec{x}_c}}{v_c}. \quad (19)$$

As a result, (16) assumes the form of the Devonshire expansion [16, 1]:

$$\begin{aligned} F - F_0(T) = & \frac{c_{\alpha\beta\gamma\delta} u_{\alpha\beta} u_{\gamma\delta}}{2} - \gamma T u_{\alpha\alpha} + 2\pi P^2 \frac{T - T_c}{C_+} - \frac{\vec{P} \vec{E}}{PE} + \frac{E^2}{8\pi} - \\ & q_{\alpha\beta\gamma\delta} P_{\alpha} P_{\beta} u_{\gamma\delta} + \frac{B_{11}}{4} \sum_{\sigma} P_{\sigma}^4 - \frac{B_{12}}{2} \sum_{\sigma > \sigma'} P_{\sigma}^2 P_{\sigma'}^2 + \frac{C_{111}}{6} \sum_{\sigma} P_{\sigma}^6 \\ & + \frac{C_{112}}{2} \sum_{\sigma \neq \sigma'} P_{\sigma}^4 P_{\sigma'}^2 + C_{123} P_1^2 P_2^2 P_3^2. \end{aligned} \quad (20)$$

In accordance with (16) - (20), the parameters of the expansion are expressed through microscopic quantities in the following manner:

$$\begin{aligned} \gamma &= \frac{i}{6} \frac{\partial}{\partial p_\alpha} \sum_{\vec{k}n} V_{ij\alpha}^{-(\vec{p}+\vec{k})\vec{k}p} G_{ij}^{\vec{k}n} \Big|_{\vec{p}=0} ; C_+ = \frac{2\lambda}{d_{11}} ; \lambda = \frac{4\pi z_c^2}{v_c} ; T_c = -\frac{2\lambda}{d_{11}} ; \\ q_{\alpha\beta\gamma\delta} &= \frac{iv_c}{z_c^2} \frac{\partial}{\partial p_\delta} V_{\alpha\beta\gamma\alpha}^{0-\vec{p}\vec{p}} \Big|_{\vec{p}=0} ; B_{\alpha\beta} = b_{\alpha\beta} + Te_{\alpha\beta} ; b_{11} = \frac{v_c^3 V_{1111}^{0000}}{6z_c^4} ; \\ b_{12} &= \frac{v_c^3 V_{1122}^{0000}}{2z_c^4} ; e_{11} = \frac{v_c^3 e_{1111}}{12z_c^4} ; e_{12} = \frac{v_c^3 e_{1122}}{4z_c^4} ; \\ c_{111} &= \frac{v_c^5 V_{111111}^{000000}}{120z_c^6} ; c_{112} = \frac{v_c^5 V_{111122}^{000000}}{24z_c^6} ; c_{123} = \frac{v_c^5 V_{112233}^{000000}}{8z_c^6} . \end{aligned} \quad (21)$$

The Greek letter indices with the subscript "a" in the potentials in (21) correspond to the acoustical degree of freedom and those without a subscript to the critical degree of freedom.

The expression of the coefficients  $\gamma$ ,  $d_{\alpha\beta}$  and  $e_{\alpha\beta\gamma\delta}$  through the microscopic parameters (17) distinguishes formulas (20) and (21) from the results of Kwok and Miller[8]. In [8] these constants are computed in approximation to the self-consistent field, which in the diagrams of Figure 1 corresponds to rejection of the summands  $1f$  and  $1j-1l$ . As noted above, those diagrams have the same order of magnitude with respect to the parameter  $T/\varepsilon_{at}$  as do the others. Moreover, in the final expressions analogous to (17) the authors of [8] suggest that on the right-hand sides the contribution of the critical degrees of freedom be completely neglected, "since their inclusion leads to components in  $F$  different from the Devonshire." Those summands correspond to the contribution to  $F$  of the region of small  $k$  and are discussed below. However, as has been mentioned, those corrections are proportional to the degree of  $T/\varepsilon_{at}$  and are small. In the principal approximation, in integrals (17), the substantial contribution comes from the region of large  $k$  and must be found by taking  $\lambda_c = 0$  in the critical denominators, after which the critical degrees of freedom introduce into the constants a contribution of the same order as do the residual ones.

The exact Green's function (12) satisfies the Dyson equation [15]:

$$G_{ij}^{-1}(\vec{k}, i\omega_n) = \left(G_0^{-1}(\vec{k}, i\omega_n)\right)_{ij} + \sum_{ij} \Sigma_{ij}(\vec{k}, i\omega_n) \quad (22)$$

where  $\Sigma_{ij}$  is the self-energy part. Graphically, the expansion of  $\Sigma$  in powers of the interaction and analogous to (15) can be written in the form

$$\Sigma = \text{a} + \text{b} + \text{c} + \text{d} + \text{e} + \text{f} + \text{g} + \text{h} + \text{i} + \text{j} + \text{k} + \text{l} + \text{m} + \text{n} \quad (23)$$

As was noted above, the anharmonic effects are substantial for the critical degrees of freedom in the region of small  $\vec{k}$ . Moreover, below the transition there appears in the crystal a piezoelectric effect that is proportional to the polarization of the linear connection of the acoustical and optical branches, it being sufficient to allow for only the connection with the critical branch. Thus,

in the matrix  $\Sigma_{ij}$  it is sufficient to find the elements  $\Sigma_{cc}$  and  $\Sigma_{ac}$  for small  $\vec{k}$  while the rest of the  $\Sigma_{ij}$  can be neglected. Comparing the analytic expressions to the diagrams of Figure 2, we obtain

$$\begin{aligned} \frac{v_c}{z_c^2} \sum_{cc}^{\alpha\beta} (0, i\omega_n) &= \delta_{\alpha\beta} \frac{v_c d_{11}(i\omega_n)}{2z_c^2} - 2q_{\alpha\beta\gamma\delta} u_{\gamma\delta} + 3 \left( b_{11} + Te_{11}(i\omega_n) \right) \\ &+ \sum_{\sigma} \delta_{\alpha\sigma} \delta_{\beta\sigma} P_{\sigma}^2 + \left( b_{12} + Te_{12}(i\omega_n) \right) \sum_{\sigma' \neq \sigma} (\delta_{\alpha\sigma} \delta_{\beta\sigma'} P_{\sigma'}^2 + \delta_{\alpha\sigma'} \delta_{\beta\sigma} P_{\sigma} P_{\sigma'}) \\ &+ 5c_{111} \sum_{\sigma} \delta_{\alpha\sigma} \delta_{\beta\sigma} P_{\sigma}^4 + c_{112} \sum_{\sigma' \neq \sigma} (\delta_{\alpha\sigma} \delta_{\beta\sigma'} P_{\sigma'}^4 + 4\delta_{\alpha\sigma} \delta_{\beta\sigma'} P_{\sigma}^3 P_{\sigma'}) \\ &+ 2c_{123} \sum_{\sigma \neq \sigma' \neq \sigma''} (\delta_{\alpha\sigma} \delta_{\beta\sigma'} P_{\sigma'}^2 P_{\sigma''}^2 + \delta_{\alpha\sigma} \delta_{\beta\sigma'} P_{\sigma} P_{\sigma'} P_{\sigma''}^2) \end{aligned} \quad (24a)$$



$$\sum_{\alpha c}^{\alpha \beta} (\vec{k}, i\omega_n) = Q^{\alpha \beta} = 2iz_c \left[ q_{12} k_\alpha P_\beta + \frac{q_{44}}{4} \left( P_\alpha k_\beta + \delta_{\alpha \beta} (\vec{k} \vec{P}) \right) \right. \\ \left. + q_a \sum_{\sigma} e_{\sigma}^{\alpha} e_{\sigma}^{\beta} (\vec{k} \vec{e}_{\sigma}) (\vec{P} \vec{e}_{\sigma}) \right]. \quad (24b)$$

Here the same notation is employed as in (17) and (21); the  $q_{ik}$  are the coefficients of electrostriction;  $q_a = q_{11} - q_{12} - q_{44}/2$  is the constant of strictional anisotropy. The amounts by which  $d_{11}(i\omega_n)$  and  $e_{\alpha\beta}(i\omega_n)$  in (24) differ from  $d_{11} = d_{11}(0)$  and  $e_{\alpha\beta} = e_{\alpha\beta}(0)$  in (17) and (21) are related to the amounts by which diagrams 2d and 2h-2n of Figure 2 differ from 1f and 1j-1l of Figure 1. In Figure 1, on those diagrams are found the Green's functions for a given value of the frequency  $i\omega_m$  over which the sum is extended. In the analogous diagrams of Figure 2, one of the  $G$  has both the internal frequency  $\omega_m$  and an external frequency  $\omega_n$ :  $G(\vec{k}, i\omega_m) \rightarrow G(\vec{k}, i\omega_m + i\omega_n)$ . However, if we do not examine the case of the very low temperatures of transition, of the order of a few degrees, then for small  $k$  the thermodynamic contribution of the summands with  $n \neq 0$  is much smaller than for  $n = 0$  and the argument of  $d_{11}$  and  $e_{\alpha\beta}$  can be omitted. We can proceed similarly with the examination set forth for the low-frequency dynamics in Section 5, when in (24)  $i\omega_n$  is replaced by the frequency  $\omega$ , i.e.,  $d_{11}(\omega) \simeq d_{11}$  and  $e_{\alpha\beta}(\omega) \simeq e_{\alpha\beta}$ , since for the large  $\vec{k}$  which are important in integrals (17) the small frequency  $\omega$  is negligible as compared with the other terms of the denominators of  $G$ .

With allowance for (22) and (24), the Green's function takes on the following form instead of (13):

$$G^{-1}(\vec{k}, i\omega_n) = \begin{pmatrix} M\omega_n^2 + A & \omega_n^2 \sqrt{\mu + V + Q} & \omega_n^2 \sqrt{\mu_r + V_r} & 0 & 0 \\ \omega_n^2 \sqrt{\mu + V + Q} & \omega_n^2 + S_0 + S & S_{cr} & i\vec{k}z_c & z_c \frac{\omega_n}{c} \\ \omega_n^2 \sqrt{\mu_r + V_r} & S_{rc} & \omega_n^2 + \lambda_r + S_{rr} & i\vec{k}z_r & z_r \frac{\omega_n}{c} \\ 0 & -i\vec{k}z_c & -i\vec{k}z_r & \frac{-v_c k^2}{4\pi} & 0 \\ 0 & -z_c \frac{\omega_n}{c} & -z_r \frac{\omega_n}{c} & 0 & \frac{v_c}{4\pi} \left( \frac{\omega_n^2}{c^2} + k^2 \right) \end{pmatrix}. \quad (25)$$

Here  $S_0$  is the sum of  $\Sigma$  and  $\lambda_c$ ; the second row and the second column correspond to the critical coordinates  $\vec{x}_c$  and the third to  $\vec{x}_r$ , and the index "c" is omitted from the critical matrices  $V$ ,  $S$  and  $\sqrt{\mu}$  for the sake of abbreviation of the notation.

The components of the matrix  $S_0$  can be expressed through the dielectric constants. Let us examine, e.g., the tetragonal phase with polarization along the  $x$ -axis. Determining the zero potential values of the strains from the minimum  $F$  condition and substituting the values found into (20) and (24), we have:

$$S_0^{\alpha\beta} = \lambda \delta_{\alpha 1} \delta_{\beta 1} \left( \frac{4\pi}{\epsilon_{11}^f} + \frac{4P^2 (q_{11} + 2q_{12})^2}{3(c_{11} + 2c_{12})} + \frac{8P^2 (q_{11} - q_{12})^2}{3(c_{11} - c_{12})} \right) + \lambda \delta_{\alpha\beta}^{\perp} \left( \frac{4\pi}{\epsilon_{\perp}^f} + P^2 \frac{q_{44}^2}{c_{44}} \right). \quad (26)$$

Here  $\delta_{\alpha\beta}^{\perp} = \delta_{\alpha\beta} - \delta_{\alpha 1} \delta_{\beta 1}$ ,  $\epsilon_{\parallel}^f$  and  $\epsilon_{\perp}^f$  are constants of the free crystal along and across the tetragonal axis. /18

In Section 5 it will be shown that the expressions in parentheses in (26) must be equal to the reciprocal susceptibilities of the pressed crystal, for which reason relation (26) could be obtained by thermodynamical means as well from the equation (38) to be given below.

Let us now discuss the correlational effects [3,14], i.e., the additional terms appearing as a result of a substitution into the right-hand sides of equations (15) and (17) for  $F$  and (23) for  $\Sigma$  of an exact Green's function instead of the  $G^{00}$  used above, corresponding to  $S_0 = Q = 0$ . We find, for example, the correction  $\delta\Sigma$  in graph 2c for  $\Sigma$  with  $\vec{k} = \omega_n = 0$ . For the sake of simplicity, we shall confine ourselves to the region below the transition temperature  $T_0$  and to the case where  $T_0$  is not too small. Under those conditions, as has been mentioned, it is sufficient to confine one's self to the classic summands with  $n = 0$  only in the sum over the frequencies  $\omega_n$  that corresponds to the internal line of the diagram:

$$\delta\Sigma_{\alpha\beta}^{(2c)}(0,0) = 3T \sum_{\vec{k}_j} V_{\alpha\beta i j}^{00 \vec{k} - \vec{k}} \left( G_{ij}(\vec{k}, 0) - G_{ij}^{00}(\vec{k}, 0) \right). \quad (27)$$

In accordance with the method of successive approximations, we take the expression (25) for the function  $G$ , while for the  $T > T_0$  under study the equations  $S_0 = 4\pi\lambda/\varepsilon_0$  and  $\varepsilon_0 = C_+(T-T_0)^{-1}$  will hold. The integral (27) converges on small  $k \sim 1/\alpha\sqrt{\varepsilon}$ , for which reason the values of  $G$  and  $G^{00}$  for small  $\vec{k}$  enter into (27). Under those conditions, the matrices  $V_b$  and  $S_{bb}$ , of (8) that describe the crossing of different branches according to (9) tend toward zero. Therefore, in  $G$  it is sufficient to take into account only the critical and acoustic branches for which the denominators of the Green's function are small at small  $\vec{k}$ ; in formula (27), however, we need consider only the critical components since the acoustic potentials  $V_{\alpha\beta\gamma\delta}^{00\vec{k}-\vec{k}}$  and  $V_{\alpha\beta\gamma\delta}^{00\vec{k}-\vec{k}}$  at small  $k$  return to zero according to (2). After we drop the electromagnetic and acoustic components,  $G_{cc}$  assumes the form:

$$G_{cc} = (S_0 + S + \lambda g^L - V^+ \frac{1}{A} V)^{-1} \quad (28)$$

where  $\lambda$  and  $g^L$  are the same as in (21) and (10). It is clear that [thanks to the long-range dipole interaction in (28)] there has appeared a linear term proportional to  $g^L$ , a coefficient at which  $\lambda$  assumes the order of the square of the plasma frequency of the ions /19 and at the small values of  $k$  under consideration there are many more residual terms of the denominator (28). Therefore, the linear degree of freedom in the region under consideration  $1/\alpha \gg k \gg 1/L$  ceases to be critical [7,19,4] and in (27) it is sufficient to take into account only the transverse components

$$\delta\Sigma_{\alpha\beta}^{(2c)} = 3T \sum_{\vec{k}} V_{\alpha\beta\gamma\delta}^{0000} \left[ \left( S_0 + S - V^+ \frac{1}{A} V \right)_t^{-1} - \left( S - V^+ \frac{1}{A} V \right)_t^{-1} \right]. \quad (29)$$

Here the indices  $(\dots)_t^{-1}$  in the matrix  $R$  mean that  $R$  must be projected on the subspace (plane) which is orthogonal with respect to  $\vec{n}$ :  $R_t = g^t R g^t$ , and therefore we employ in this subspace the matrix inverse to  $R_t$ . The values of the elements  $R_t^{-1}$  can be found from the matrix  $(R + \lambda g^L)^{-1}$  if we make  $\lambda \rightarrow \infty$ :

$$(R_t^{-1})_{\alpha\beta} = \frac{1}{\sum_{\mu\nu} n_\mu n_\nu A_{\mu\nu}(0)} \frac{\partial}{\partial \xi} A_{\alpha\beta}(\xi) \Big|_{\xi=0} \quad (30)$$

where  $A_{\alpha\beta}(\xi)$  is the algebraical supplement of the matrix element  $R_{\alpha\beta} + \xi n_\alpha n_\beta$ .

If in (29) we substitute (9) for  $S, V, A$  and introduce the new

variable  $x = |\vec{k}| \sqrt{\epsilon_0/\lambda}$  with integration over  $\vec{k}$ , the integral (29), assuming cubic symmetry, can be converted to the form:

$$\delta \Sigma_{\alpha\beta}^{(2c)} = - \delta_{\alpha\beta} \frac{4\pi\lambda T}{\sqrt{\epsilon_0}} J_{2c}, \quad (31)$$

where

$$J_{2c} = \frac{3}{2^6 \pi^5} \lambda^{3/2} (b_{11} + 2b_{12}) \int_0^\infty dx \int d\vec{n} \operatorname{Sp} \left[ (1 + x^2 \phi)^{-1} \phi_t^{-1} \right], \quad (32)$$

$$\phi = s_t g^t + s_a g^a - (v_t g^t + v_a g^a) (a_l g^l + a_t g^t + a_a g^a)^{-1} (v_t g^t + v_a g^a),$$

$g^i$ ,  $b_{\alpha\beta}$  are the same as in (10) and (20), and  $d\vec{n}$  represents integration over the vector angles  $\vec{n}$ .

The correction for the graph 2d is calculated similarly. However, the result assumes the form (31), and the corresponding constant  $J_{2d}$  is proportional to the square combinations of the striction constants  $q_{ik}$  divided into the modulus of elasticity  $C_{ik}$ .

Since we have to keep in mind the relatively small size of  $b_{\alpha\beta}$ , a quantitative calculation must also take into account some graphs which are omitted from Figure 2, i.e., the graphs 2f...2n in which two dotted lines are replaced by one solid line. The insertion of these terms leads to a substitution in (32)  $b_{\alpha\beta} \rightarrow T n_{\alpha\beta}$ , where the values  $L_{\alpha\beta} \sim e_{\alpha\beta}$  in (20).

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The components  $\lambda G_{cc}$ , according to (38) below, are equal to the dielectric permeability  $\epsilon$ . Hence, the formula for  $\epsilon$  with corrections of the first approximation assumes the form:

$$\epsilon = (1/\epsilon_0 - JT/\sqrt{\epsilon_0})^{-1} \simeq \frac{C_+}{T-T_c} \left( 1 + JT \sqrt{\frac{C_+}{T-T_c}} \right) \quad (33)$$

where the value  $J$  is equal to the sum of the terms of the form (32) given above.

The correction term in (33) assumes the conventional form characteristic for corrections to a zero approximation of a self-consistent field [14,3]. The correction terms for other thermodynamic values as well have an analogous form [3]. The constant  $J$  in order of value is equal to the inverse atomic energy  $1/\epsilon_{at}$ ; therefore, as we have already mentioned, the principal parameter determining the suitability of the zero approximation (20) and (25) and the small size of the correlation effects is  $T/\epsilon_{at}$ .

Let us estimate the correction term in (33) for  $\text{BaTiO}_3$ . In this material  $b_{\alpha\beta} Te_{\alpha\beta}$  and  $q_{ik}^2/c_{ik}$  are the values of one order so that for estimating  $J$  we can use (32). The value  $\lambda$  is inserted into the formula for the spectrum of the critical vibrations (41) and we can conclude from a comparison with the data in [17] that  $\sqrt{\lambda} \sim 10^{13}$  Hz. The data with reference to  $s_i$  and  $v_i$  in  $\text{BaTiO}_3$  are unknown, but in  $\text{SrTiO}_3$   $s_i \sim a_i$  [18], so that we can expect the same thing in this case as well. If we use for  $b_{\alpha\beta}$  and  $a_i$  the values given in [1], we will have

$$J \sim \frac{3}{32\pi^3} \frac{\lambda^{3/2}(b_{11} + 2b_{12})}{s_t^{3/2}} \sim \frac{1}{70_{\text{ev}}} ; JT \sim 5 \cdot 10^{-4} \quad (34)$$

At the transition point, the correction term  $JT\sqrt{\epsilon_0}$  in (33) amounts to about 5%.

## 5. SPECTRUM OF VIBRATIONS AT SMALL $\vec{k}$

The dynamic properties of the system can be described satisfactorily by using the Green's time function [15]  $G(t)$ :

$$G_{ij}^{(t)}(\vec{r}_1 t_1, \vec{r}_2 t_2) = \langle \hat{T} \left( \xi_i(\vec{r}_1 t_1) - \bar{\xi}_i \right) \left( \xi_j(\vec{r}_2 t_2) - \bar{\xi}_j \right) \rangle ; \quad (35)$$

$$\xi_i(t) = e^{iHt} \xi_i e^{-iHt}.$$

The Fourier component of the time function  $G^{(t)}(\vec{k}, \omega)$  can be found from the temperature function  $G(\vec{k}, i\omega n)$  (12) by means of an analytical extension with discrete number of points  $i\omega n$  in the complex plane  $\omega$  on the real axis [15]:

$$G^{(t)}(\vec{k}, \omega) = G(\vec{k}, \omega) \quad (36)$$

Hence, in the approximation  $G^{(t)}$  under consideration, we obtain matrix (25) by the exchange  $\omega_n \rightarrow -i\omega$ .

The excitation spectrum is determined by the  $G^{(t)}$  poles, i.e., the frequency values at which there is a solution in the corresponding systems of similar equations [15], where the characteristic vectors  $\xi_i$  determine the amplitudes of the displacement in the excitation. If we shift from the potential component to the electrical field  $\vec{e}$  for the sake of clarity, we will have for the determination of the spectrum the equations

$$(A - \mu\omega^2)\vec{u} + (V + Q - \omega^2\sqrt{\mu})\vec{x}_e + (V - \omega^2\sqrt{\mu}_r)\vec{x}_r = 0$$

$$(V^+ + Q^+ - \omega^2\sqrt{\mu})\vec{u} + (S_0 + S - \omega^2)\vec{x}_e + S_{er}\vec{x}_r - z_e\vec{E} = 0$$

$$(V_r^+ - \omega^2\sqrt{\mu}_r)\vec{u} + S_{re}\vec{x}_e + \left[ (\lambda_r - \omega^2)\delta_{rr'} + S_{rr'} \right] \vec{x}_{r'} - z_r\vec{E} = 0$$

$$\frac{4\pi\omega^2}{v_e} (z_e\vec{x}_e + z_r\vec{x}_r) + \left( \frac{\omega^2}{c^2}\delta_{\alpha\beta} - k^2\delta_{\alpha\beta} + k_\alpha k_\beta \right) E_\beta = 0. \quad (37)$$

System (37) differs from the conventional equations of harmonic vibrations by the existence of a dependence on temperature and deformation in the values of  $S_0$  and  $Q$ . These equations are very

clear, and analogous semiphenomenological relationships were written previously by Ginsburg [9,14] and Cochran [10,11]; who called them "a linear anharmonic approximation". These equations have been given above microscopically, and the regular method used makes it possible also to investigate higher approximations in terms of the parameter  $T/\varepsilon_{at}$  and (to a certain degree) the effects of damping [4] as well.

In regions of small  $k$  and  $\omega$  the relationship between the critical and acoustical branches with other branches in (37) is small, and the components  $\vec{x}_r$  can be disregarded; for  $A, V, S$  and  $Q$ , however, expansions (9) and (24b) are used.

In the case where we are considering macroscopic wavelengths /22 greater than or on the order of the dimensions of the crystal  $L$  the vector  $\vec{k}$  in (37) must be substituted for the differentiation operator  $\partial/\partial\vec{R}$  in (37) is changed into a set of equations for the theory of elasticity and electrodynamics [19], taking account of the piezoelectric effect below  $T_0$ . We can see from (37) that when we consider the vibrations in a uniform field  $\vec{E}$ , the piezoelectric bond of the critical branch, which determines the polarization, becomes significant only for the frequencies  $\omega \lesssim 1/L\sqrt{\alpha_i}$ , i.e., in the region of piezoacoustic resonances. At high frequencies, the link between the branches falls as  $1/\omega^2$ , so that the value of  $S_0$  in (37) determines the dielectric permeability  $\varepsilon$  at those high frequencies, which is called the permeability of the pressed crystal:

$$\varepsilon_{\alpha\beta} = \lambda(S_0^{-1})_{\alpha\beta} ; S_0 = \lambda/\varepsilon \quad (38)$$

After omitting the component  $\vec{E}$ , the equations for the spectrum at small  $\vec{k}$  and  $\omega$  assume the form

$$\begin{aligned} (A - M\omega^2)\vec{u} + (V + Q - \omega^2\sqrt{\mu})\vec{x}_c &= 0 \\ (V + Q^+ - \omega^2\sqrt{\mu})\vec{u} + \left(\frac{\lambda}{\varepsilon} + S - \omega^2 + \lambda g^L - \lambda g^t \frac{\omega^2}{c^2 k^2 - \omega^2}\right)\vec{x}_c &= 0. \end{aligned} \quad (39)$$

If we do not take into account the very long waves  $1/k \approx 10^{-3}$  cm, where there is a definite crossing of the phonon and electromagnetic branches [20,4], then the relativistic transverse term in (39) can be disregarded. Of the remaining six branches, one which is linear optic assumes the high frequency  $\omega \sim \sqrt{\lambda}$  and will not be considered, since at the transition from (37) to (39) the frequencies are considered small. Therefore, in (39), there remain only the transverse critical coordinates and the equation for the spectrum can be written in the form

$$\text{Det} || A - M\omega^2 + (V + Q - \omega^2\sqrt{\mu})\left(\frac{\lambda}{\varepsilon} + S - \omega^2\right)_t^{-1}(V + Q^+ - \omega^2\sqrt{\mu}) || = 0, \quad (40)$$

where the designation  $(\dots)_t^{-1}$  is the same as in (29) and (30).

Thanks to the transversality of the critical matrix, the linear parts of matrices  $S$ ,  $V$  and  $Q$  do not make any contribution to (40). Therefore, in matrix  $Q_{\alpha\beta}$  (24b) it is possible to omit the term

which is proportional to  $k_\beta$ , and in matrices  $V$  and  $S$  (9) to insert /23

$v_L = v_t$  and  $s_L = s_t$ . After this, in the system of the principal axes of the crystal,  $V$  and  $S$  will be diagonal. At known elastic striction and dielectric constants, the spectrum of the five branches, given in (40), is determined by the six constants  $\lambda$ ,  $\mu$ ,  $s_t$ ,  $s_a$ ,  $v_t$  and  $v_a$ , and its experimental investigation makes it possible to find these constants. Let us note, however, that since the coordinate of any of the ions of the cell can be chosen as the acoustic coordinate, the regeneration of these constants in Section 2 along the spectrum is not completely unambiguous. The vibrational frequencies are expressed only by such combinations of  $\lambda$ ,  $\mu$ ,  $s_i$  and  $v_i$  which are independent of the indicated choice. Therefore, a complete spectral analysis makes it possible to determine only certain possible groupings of the constants (according to the number of nonequivalent atoms in the cell).

The five branches described in (40) at the very smallest values of  $\vec{k}$  can be divided into three acoustic branches with linear dependence of  $\omega$  upon  $k$ , and two transverse critical branches with

a gap in the spectrum which is proportional to  $\epsilon^{-\frac{1}{2}} \sim |T - T_c|^{\frac{1}{2}}$ . Thus, in the tetragonal phase we have

$$\omega_{c1}^2(0) = \frac{\lambda}{(1-\mu/M)\epsilon_{\perp}} ; \quad \omega_{c2}^2(0) = \frac{\lambda}{1-\mu/M} \left( \frac{n_1^2}{\epsilon_{\perp}} + \frac{n_{\perp}^2}{\epsilon_{11}} \right) \quad (41)$$

Aside from the temperature dependence of this gap, the essential property of this spectrum consists in that it changes considerably with wavelengths which are much greater than the interatomic distances  $a$ . Thus, in the region  $1/a \gg k \gg \omega_c(0)(\sqrt{a_i})^{\frac{1}{2}}$  we can disregard  $S_0$  and  $Q$  in (40) and all five branches will have a linear dependence of  $\omega$  upon  $k$ . With  $k \sim \omega_c(0)a_i^{-\frac{1}{2}}$ , there is a sharp break in the dependence of the acoustic frequencies upon  $k$ , and the velocities of sound at small and large frequencies do not agree.

For the sake of illustration, let us consider the partial cases in (40). If  $\vec{k}$  is directed along  $x$ , then the five branches (40) will be divided into one linear acoustic branch and two pairs of degenerate transverse vibrations. However, if  $\vec{k}$  is directed along the principal axis, perpendicular to the tetragonal axis, we will have only one pair of branches whose polarization is perpendicular to  $\vec{k}$  and  $\vec{P}$ , while the remaining transverse branches below  $T_0$  will be combined with the linear, and the dispersion equation will become cubic:

$$1) \quad n_1 = 1, n_{\perp} = 0: \quad \omega_l^2 = k^2(a_l + a_a) \quad /24$$

$$(k^2 a_t - \omega^2)(k^2 s_t - \omega^2 + \frac{\lambda}{\epsilon_{\perp}}) - (k^2 v_t - \omega^2 \sqrt{\mu/M})^2 - \frac{\lambda P^2 q_{44}^2}{16\pi\rho} k^2 = 0$$

$$2) \quad n_2 = 1, n_1 = n_3 = 0: \quad (k^2 a_t - \omega^2)(k^2 s_t - \omega^2 + \frac{\lambda}{\epsilon_{\perp}}) -$$

$$(k^2 v_t - \omega^2 \sqrt{\mu/M})^2 = 0 \quad (42a)$$

$$\left[ k^2(a_l + a_a) - \omega^2 \right] \left[ (k^2 a_t - \omega^2)(k^2 s_t - \omega^2 + \frac{\lambda}{\epsilon_{11}}) -$$

$$(k^2 v_t - \omega^2 \sqrt{\mu/M})^2 \right] - (k^2 a_t - \omega^2) \frac{\lambda P^2 q_{12}^2 k^2}{\pi\rho} = 0.$$

(42b)



To illustrate the angular dependence of the spectra below  $T_0$ , let us consider the hypothetical case of a crystal in which we have the constants  $a_a = v_a = s_a = 0$  in (9). In  $\text{BaTiO}_3$ , for example, the constant of angular anisotropy  $a_a$  is of an order such that  $a_t$  and  $a_l : a_a : a_t : a_l = 0.6 : 0.44 : 2.2$ . At the values under discussion, this anisotropy is usually insignificant. In this case it is preferable to carry out the calculation in a system of coordinates where one of the axes is directed along  $\vec{k}$ , and the other is perpendicular to  $\vec{k}$  and  $\vec{P}$ . Then we again have a pair of branches with a polarization perpendicular to  $\vec{k}$  and  $\vec{P}$  and for others we obtain an equation of the third degree:

$$\begin{aligned}
 & (k^2 a_t - \omega^2)(k^2 s_t - \omega^2 + \frac{\lambda}{\epsilon_{\perp}}) - (k^2 v_t - \omega^2 \sqrt{\mu/M})^2 - \\
 & \frac{\lambda P^2 k^2 n_1^2}{\pi \rho} \left( \frac{q_{44}}{4} + q_a n_{\perp}^2 \right)^2 = 0 \\
 & (k^2 a_l - \omega^2) \left[ (k^2 a_t - \omega^2)(k^2 s_t - \omega^2 + \frac{\lambda n_{\perp}^2}{\epsilon_{11}} + \frac{\lambda n_l^2}{\epsilon_{\perp}}) \right. \\
 & \left. - (k^2 v_t - \omega^2 \sqrt{\mu/M})^2 \right] - \frac{\lambda P^2 k^2}{\pi \rho} \left[ (k^2 a_l - \omega^2) n_1^2 \left( \frac{q_{44}}{4} + q_a n_{\perp}^2 \right)^2 \right. \\
 & \left. + (k^2 a_t - \omega^2) n_{\perp}^2 (q_{12} + q_a n_l^2)^2 \right] = 0. \tag{43}
 \end{aligned}$$

In  $\text{BaTiO}_3$ ,  $\epsilon_{\perp}$  is much greater than  $\epsilon_{\parallel}$ , and  $q_a$  is a constant  $q_{12}$ ,  $q_{44}/4$  such that the anisotropy of the spectrum below  $T_0$  is significant.

The formulas in this section were obtained by disregarding the relaxation processes. Frequently they correspond to isothermal vibrations; at the same time, depending on the relationship between  $k$ ,  $\omega$  and the coefficients of thermoconductivity and persistence of the oscillation, they can also be adiabatic [1]. However, these effects are proportional to the higher degrees of  $T/\epsilon_{at}$  and are small; for example, in  $\text{BaTiO}_3$  the difference between the adiabatic dielectric permeability and the isothermal permeability amounts to about 3% [1]. The damping of the vibrations in the ideal crystal under consideration is also proportional to the higher degrees of the anharmonicity of  $T/\epsilon_{at}$ , and (as estimates will show) they are small. Therefore, the large value for the width of the crystal vibrations which was observed [17] and the dielectric losses at ultra- /25

high frequencies [1] are apparently related to the scattering at crystal defects. These problems will be discussed in greater detail in another paper.

## 6. CONCLUSION

In conclusion, we would like to make two observations, one of which is methodical and the other is of an experimental character.

Let us consider the relationship of this paper to a description of transition using the method of the self-consistent field [3,4]. In [3,4], the radius of interaction  $r_0$  of ions of different cells was assumed to be large. Therefore, the interaction is described well by the mean self-consistent field, and the correlation of effects were proportional to  $r_0^{-3}$ . In this paper, the small parameters are the anharmonicity  $T/\epsilon_{at}$  and the abnormally low degree of rigidity  $\lambda_c \sim \lambda_r T/\epsilon_{at}$ . The anharmonic correlation effects are significant only for phonons with low  $k \sim \frac{1}{a} \sqrt{T/\epsilon_{at}}$ ; the motion of the remaining phonons can be considered harmonic and independent of transition. Therefore, in calculating the field acting on a given ion, an important contribution is made by the noncritical phonons. The field can be considered independent of the position of the ion and can be replaced by an average value, disregarding correlation. Thus, the approximation used is analogous to the approximation of the self-consistent field; only in [3,4] was use made of the small degree of correlation between the particles in a different cell.

Here, with low anharmonicity, phonons with different  $\vec{k}$  are independent of one another. Therefore, the general results and the form of the temperature relationships (20), (33), (41) remain the same as in [3,4] and the phenomenological theories [16,19,14,10]. There is only a change in the expression of the phenomenological constant through microparameters: in [3,4] they were expressed through the mean temperatures for independent particles, while in this case they are expressed by the averages for independent phonons. This is explained by the fact that in the models of Devonshire [16] and Slater [6], who used the method of the self-consistent field, the same results were obtained (agreeing with experiment) as in weak anharmonicity [7]. In this connection, the theory expressed in [4], stating that the success of the phenomenological theory for perovskites indicates a large  $r_0$  of these systems, does not appear to be necessary and sufficient; a much more likely explanation would be the small size of  $\lambda_c$  and the weak anharmonicity.

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From the physical standpoint, the case of the applicability of the method of the self-consistent field and the solution according to anharmonicity are different. For the former, we require a large radius  $r_0$ ; anharmonicity, on the other hand, can be arbitrarily large and can frequently be a case of an order-disorder transition

[3,4]. The regions of applicability can of course overlap; for example, at large  $r_0$  the value of  $s_t$  in (34) is proportional to  $r_0^2$  and the correlational correction is proportional to  $r_0^{-3}$ .

A second remark is directed toward the structure of the crystals under consideration. As we have pointed out, the constants  $e_{\alpha\beta}$ ,  $c_{\alpha\beta\gamma}$  in (20) in perovskites are abnormally large relative to the constant of the first approximation  $b_{\alpha\beta}$ ; this is partially responsible for the closeness of the transition of the first type to the second. In accordance with formulas (21) and (17), this means that the critical potentials  $V^{(6)}$  in the corresponding atomic units are much greater than the potentials  $V^{(4)}$ . Large values of  $V^{(6)}$  can be related to a known feature of the structures: a dense packing with very small "free space" for relative transitions of the ions [1]. This can lead to a sharp increase in repulsion at small values of  $x_c$ , i.e., a situation of the type of a rectangular hole. In this connection, it would be very interesting to determine the microscopic potentials of  $V^{(n)}$  in (21), i.e., the constants  $z_c$  or  $\lambda_c$ , which (as we found in Section 5) can be achieved by investigating the dynamics. It would also be very desirable to find transitions of the displacement type in other nonferroelectrics and non-oxygen-octahedral crystals, since it is clear from what has been stated above that the characteristics of thermodynamics and transition dynamics of displacement type are not at all related to ferroelectricity and may have a general character.

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## REFERENCES

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1. Iona, F. and D. Shirane: Segnetoelektricheskiye kristally (Ferroelectric Crystals), Mir (Moscow), 1965.
2. Vaks, V. G. and A. I. Larkin: Zhur. Eksptl. i Teoret. Fiz., Vol. 49, p. 975, 1965.
3. Vaks, V. G., A. I. Larkin and S. A. Pikin: Zhur. Eksptl. i Teoret. Fiz., Vol. 51, p. 361, 1966.
4. Vaks, V. G., V. M. Galitskiy and A. I. Larkin: Zhur. Eksptl. i Teoret. Fiz., Vol. 51, p. 1592, 1966.
5. Hill, R. M. and S. K. Tchiki: Phys. Rev., Vol. 128, p. 1140, 1962; Vol. 132, p. 1603, 1963.
6. Slater, J. C.: Phys. Rev., Vol. 78, p. 748, 1950.
7. Anderson, P. W.: Fizika dielektrikov (Physics of Dielectrics), Izdatel'stvo AN SSSR (Moscow), 1960, 290 p.
8. Kwok, P. C. and P. B. Miller: Phys. Rev., Vol. 151, p. 387, 1966.
9. Ginzburg, V. L.: Zhur. Eksptl. i Teoret. Fiz., Vol. 19, p. 36, 1949; Uspekhi Fiz. Nauk, Vol. 38, p. 490, 1949.

10. Cochran, W.: Adv. Phys., Vol. 9, p. 387, 1960.
11. Cochran, W.: Adv. Phys., Vol. 10, p. 401, 1961.
12. Silverman, B. D. and R. J. Joseph: Phys. Rev., Vol. 129, p. 2062, 1963; Vol. 133, p. A207, 1964; Silverman, B. D.: Phys. Rev., Vol. 135, p. A1596, 1964.
13. Cowley, R. A.: Phil. Mag., Vol. 11, p. 673, 1965.
14. Ginzburg, V. L.: Fiz. Tverd. Tel., Vol. 2, p. 2031, 1960.
15. Abrikosov, A. A., L. P. Gor'kov and I. E. Dzyaloshinskiy: /28  
Metody kvantovoy teorii polya v staticheskoy fizike (Methods  
of Quantum Field Theory in Statistical Physics), Fizmatgiz  
(Moscow), 1962.
16. Devonshire, A. F.: Phil. Mag., Vol. 40, p. 1040, 1949; Vol. 42,  
p. 1065, 1951.
17. Ballantyne, J.: Phys. Rev., Vol. 136, p. A429, 1964.
18. Cowley, R. A.: Phys. Rev., Vol. 134, p. A981, 1964.
19. Landau, L. D. and E. M. Lifshits: Elektrodinamika sploshnykh  
sred (Electrodynamics of Dense Media), Gostekhizdat (Moscow).  
1957.
20. Born, M. and K. Khuan: Dinamicheskaya teoriya kristallicheskikh  
reshetok (Dynamic Theory of Crystal Lattices).

# THERMAL OSCILLATIONS AND THE MÖSSBAUER EFFECT IN THE REGION OF PHASE TRANSITIONS IN FERROELECTRICS

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*ABSTRACT: Anomalies of thermal vibrations and the probability of Mössbauer absorption in the vicinity of the phase transitions are discussed for the case of ferroelectrics. For transitions of displacement type, the anomalies are expressed by dielectric characteristics and certain constants which are determined by the low-frequency spectrum of the crystal. Anisotropy of the vibrations below the transition was found. Estimates of the anomalies are made for order-disorder transitions.*

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## 1. INTRODUCTION

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In Part I of this collection [1], we discussed the thermodynamics and low-frequency spectra of vibrations in phase transitions of displacement type in ferroelectrics. In the present paper, the methods which were developed there will be applied to a description of the thermal vibrations and the mean quadratic displacement in the vicinity of the transition. These values can be investigated experimentally by x-rays or neutronographs [2], but the accuracy obtained is evidently insufficient for studying the thermal relationships. Thermal vibrations have recently been investigated in ferroelectrics in a number of experimental papers, employing the Mössbauer effect [3,4], and anomalies were detected in the Debye-Waller factor in the vicinity of the transition. Theoretical evaluation of these experiments has thus far been limited to general theories about the possible influence of the critical vibration [5], without any attempt at a quantitative calculation. A more detailed study of this paper shows that in the effect observed, along with the temperature dependence of the critical frequency, there was also a significant piezoelectric effect and a difference between the phase transitions of the first and second types. The resulting expression for the anomalous frequency of the average displacement, on the basis of known dielectrics, dielectric striction and angular constants, contains several constants which characterize the critical vibrations and the degree of participation of a given ion. The same constants determine the spectrum of the low-lying excitations [1], so that by using the Mössbauer effect it was possible to gain

an idea about these fundamental characteristics of the crystal. The temperature relationship of the anomaly above the transition is inversely proportional to the root of the dielectric permeability  $\epsilon$ , while below the transition it is expressed by  $\epsilon$  and the spontaneous polarization  $P$ . /32

As in [1], we are discussing an ideal crystal. For the sake of an example, we are making our estimates essentially on perovskites, with transition from the cubic to the tetragonal phase, although the general formulas are frequently applicable to any nonferroelectric transition of displacement type. Section 4 discusses several theories and estimates for the Mössbauer effect in the vicinity of phase transitions of order-disorder type. In this case, the nature of the anomaly in the Debye-Waller factor depends on the relationship between the natural width of the Mössbauer line to the relaxation time of the ions in the cells and the equilibrium distribution.

## 2. GENERAL FORMULAS FOR THE PROBABILITY OF MÖSSBAUER ABSORPTION

The conventional expression for the probability of Mössbauer absorption  $W$  by the thermal Debye-Waller factor [6] is obtained by using a harmonic approximation for the lattice vibration. In the vicinity of the phase transition, there are effects of anharmonicity; therefore, we select an expression for  $W$  which is somewhat more general than the usual one.

The probability of the absorption of a quantum with the frequency  $\omega$  in the Mössbauer effect is determined by the expression [6,7]:

$$W(\omega) = \frac{\sigma_0 \Gamma}{2\pi} \int_{-\infty}^{\infty} e^{i(\omega - \omega_0)t - \Gamma|t|} \langle e^{i\vec{q}(\vec{u}_{\vec{r}}(t) - \vec{u})} e^{-i\vec{q}(\vec{u}_{\vec{r}}(0) - \vec{u})} \rangle dt. \quad (1)$$

Here  $\omega_0$  is the resonance frequency,  $\Gamma$  is the natural width of the nuclear level,  $\vec{q}$  is the quantum wave vector,  $\vec{u}_{\vec{r}}(t) - \vec{u}$  is the Heisenberg operator for the nucleus displacement relative to the equilibrium position  $\langle \vec{u}_{\vec{r}} \rangle = \vec{u}$ :

$$\vec{u}_{\vec{r}}(t) = e^{iHt} \vec{u}_{\vec{r}} e^{-iHt}.$$

$H$  is the usual phonon Hamiltonian of the crystal [see, e.g., (1.1) and (1.9)]. The sign  $\langle \dots \rangle$  indicates a statistical average:

$$\langle \dots \rangle = \frac{Sp(\dots) \exp(-\beta H)}{Sp \exp(-\beta H)}; \quad \beta = 1/T;$$

where  $\sigma_0$  is the absorption cross section. /33

In the case under consideration, involving transitions of displacement type, the times which characterize the motion of the absorbing ion have the order of the inverse optical frequencies and are significantly less than the emission times  $1/\Gamma \gtrsim 10^{-9}$  sec. Therefore, the expression in angular brackets in (1), before being integrated over  $t$ , can be averaged over the time; then the average over the time, on the basis of the general theorems, can be statistically replaced by the statistical mean. As a result, we obtain

$$W(\omega) = \frac{\sigma_0}{\pi} f^2 \frac{\Gamma}{(\omega - \omega_0)^2 + \Gamma^2}, \quad (2)$$

where the thermal Debye-Waller factor is given by the expression

$$f = |\langle e^{i\vec{q}(\vec{u}_r - \bar{\vec{u}})} \rangle|. \quad (3)$$

In Formulas (1) to (3), we have disregarded the presence of spin in the nucleus and the effects of quadrupole and magnetic splitting affiliated with it. This splitting can be equated in value with the line width, but is always much smaller than the optical frequencies. Consideration of these splittings leads to the fact that instead of (1) we will have the sum of several terms with frequencies depending on the spin constant of the nucleus. If we integrate this equation over a frequency range which is large relative to the line width but small relative to the optical frequencies, we will find that the complete probability of the Mössbauer transition, as in the case described (2), will be equal to  $\sigma_0 f^2$ .

The factor  $f$  in (3) is calculated simply in the harmonic approximation, which (as it will be recalled) is not directly applicable to the transition region. However, for displacement-type transitions, the anharmonicity is small [1]; this makes it possible to obtain a number of successive approximations for the thermal factor as well as for the thermodynamic values.

If we expand expression (3) in a series according to the powers of the exponent, we obtain: /34

$$f = 1 - \frac{q^2}{2} \langle (u - \bar{u})^2 \rangle + \frac{q^4}{4!} \langle (u - \bar{u})^4 \rangle - \dots \quad (4)$$

where  $u$  expresses the projection of  $\vec{u}_r$  in the direction  $\vec{q}$ .

The second term in (4) is expressed by the thermal Green's function [8,1]  $G(\vec{k}, i\omega_n)$  as follows:

$$\langle (u_r^\alpha - \bar{u}^\alpha)(u_r^\beta - \bar{u}^\beta) \rangle = T \sum_{\vec{k}n} G_{\alpha\beta}(\vec{k}, i\omega_n). \quad (5)$$

The third term is expressed by the two-phonon Green's function  $K$ , which satisfies the Bethe-Salpeter equation [8], which can be written symbolically in the form

$$K = GG + GG\hat{\Gamma}K \quad (6)$$

where  $\hat{\Gamma}$  is the amplitude of the two-phonon scattering.

By using the method given in Section 4 of [1], we can see that the relationship of the second term (6) to the first is proportional to the relationship of the temperature  $T$  to the atomic energy  $\varepsilon_{at}$ , i.e., to the parameter of anharmonicity. Therefore, the second term (6) can give a significant indication in (4) only at very large values of  $q$ , when the complete probability  $W \sim \exp(-q\langle|u-\bar{u}|^2\rangle)$  is much less. At not too high values of  $q$  in (6), it is sufficiently limited by the first term, so that the third term (4) assumes the form

$$\frac{1}{8} \left[ q_\alpha q_\beta T \sum_{\vec{k}n} G_{\alpha\beta}(\vec{k}, i\omega_n) \right]^2. \quad (7)$$

Similarly, we calculate the remaining terms of the expansion (4). As a result, we obtain

$$f = \exp \left[ -\frac{1}{2} q_\alpha q_\beta \langle (u_\alpha - \bar{u}_\alpha)(u_\beta - \bar{u}_\beta) \rangle \right] \quad /35$$

$$\langle (u_\alpha - \bar{u}_\alpha)(u_\beta - \bar{u}_\beta) \rangle = \langle u_\alpha u_\beta \rangle - \bar{u}_\alpha \bar{u}_\beta = T \sum_{\vec{k}n} G_{\alpha\beta}(k, i\omega_n).$$

Expression (8) has a general form [6], but the average and  $G$  in (8) correspond to the Green's function with anharmonicity taken into account. This formula, as well as the analogous results in [1], can be obtained if we use the "linear anharmonic approximation" [9], in which we use the formulas of the harmonic theory, but we introduce the temperature dependence phenomenologically into the Green's function; in the first approximation for  $T/\varepsilon_{at}$ , such a method is correct.

### 3. ANOMALIES OF THE THERMAL VIBRATIONS IN TRANSITIONS OF DISPLACEMENT TYPE

The matrix  $G_{\alpha\beta}$  in (8) for the case under consideration can be obtained from (1.25):

$$G^{-1}(k, i\omega_n) = M\omega_n^2 + A - \sum_{b, b'} \left( \omega_n^2 \sqrt{\mu_b} + V_b + Q_b \quad \omega_n^2 + S_0^{(b)} + S_{bb'} \right. \\ \left. + \frac{4\pi z_b z_{b'}}{v_c} g^{l-1} \right) \left( \omega_n^2 \sqrt{\mu_{b'}} + V_{b'} + Q_{b'} \right). \quad (9)$$



Here the subscripts  $b, b'$  mark the different optical coordinates: the critical  $\vec{x}_c$  and the remaining  $\vec{x}_r$ ,  $\omega_n = 2n\pi T$  are the discrete frequencies of the temperature diagram of the technique [8], the constants  $\mu_b$  and  $z_b$  characterize the completely effective masses and the polarizability of the optical branches,  $v_c$  is the volume of an elementary cell,  $g_{\alpha\beta}^l = n_\alpha n_\beta$ ,  $\vec{n} = \vec{k}/k$ . The constants  $S_0^{(b)}$  are proportional to the squares of the optical frequencies at  $k \rightarrow 0$ , so that for a critical coordinate, the  $S_0^{(c)}$  matrix which is the reverse of the matrix of the dielectric permeabilities of the compressed crystal  $\epsilon$  is:

$$S_0^{(c)} \equiv S_0 = \lambda/\epsilon; \quad \lambda = \frac{4\pi z_c^2}{v_c}. \quad (10)$$

The matrices  $A, V$  and  $S$  at small  $k$  are given by (1.9) and are proportional to  $k^2$ , while the piezoelectric matrix  $Q$  according to (1.24b) is proportional to  $k$  and the polarization  $P$ . /36

If the temperature is not low relative to the Debye temperature  $\theta_D$ , then in the interval over  $\vec{k}$  in (8) the principal contribution is made by the region of large  $\vec{k}$ , of the order of the inverse lattice constant  $1/a$ ; the contribution of the region of small  $k$  is given by the statistical weight  $\sim k^3$ . However, this principal contribution is a smooth function of temperature and does not have any peculiar feature in the vicinity of the transition. As stated in [1], the critical phenomena are important only in the range of the small wave vectors  $k \sim 1/a\sqrt{\epsilon}$ . Therefore, in order to find the anomalous portion of the displacement from the function  $G(\vec{k}, i\omega_n)$  in (8), we can calculate the function which is regular in the vicinity of the transition  $G_{00}(\vec{k}, i\omega_n)$ , obtained from  $G$  by the substitution  $S_0 = Q = 0$ . The corresponding anomalous portion of the displacement will be  $\langle u_\alpha u_\beta \rangle_c$ :

$$\langle u_\alpha u_\beta \rangle_c = T \sum_{n\vec{k}} \left( G(\vec{k}, i\omega_n) - G^{00}(k, i\omega_n) \right)_{\alpha\beta}. \quad (11)$$

In integral (11), the region of small  $k \sim 1/a\sqrt{\epsilon}$  is significant. Therefore, in (9) we can make use of the expansion of the matrices which enter into it for small  $k$ . Then, as in Sections 4 and 5 of [1], we can disregard the contribution of all normal optical branches  $\vec{x}_r$  as well as the longitudinal critical branch  $\vec{x}_c \vec{k} | \vec{n}$ . In addition, if we do not consider the case of extremely small  $T$ , the temperature frequencies  $\omega_n = 2n\pi T$  in (9) and (11) is much greater than the critical frequencies  $\omega_c \sim (\lambda/\epsilon)^{1/2}$ , and in summation over  $n$  in (11) it is sufficient to replace the classical term with  $n = 0$ . As a result, we will have:

$$\langle u_\alpha u_\beta \rangle_c = T \sum_{\vec{k}} \left[ \frac{1}{A - (V+Q) \left( \frac{\lambda}{\varepsilon} + S \right)_t^{-1} (V+Q^+)} - \frac{1}{A - V S_t^{-1} V} \right]_{\alpha\beta} \quad (12)$$

Here, as in [1], the matrices  $V$ ,  $S$  and  $Q$  without subscripts correspond to the critical branch while  $R_t^{-1}$  [according to (1.30)] stands for the projection of the matrix  $R$  into subspace, orthogonal to  $\vec{n}$ , and the matrices taken in this subspace, the reverse of that obtained:

$$R_t^{-1} = \frac{1}{\sum_{\mu, \nu} n_\mu n_\nu A_\nu(0)} \frac{\partial}{\partial \xi} A_{\alpha\beta}(\xi) \Big|_{\xi=0} \quad (13) \quad /37$$

where  $A_{\alpha\beta}(\xi)$  is the algebraic component of the matrix element  $R_{\alpha\beta} + \xi n_\alpha n_\beta$ .

We will show that in the region above the transition temperature  $T_0$ , the anomalous portion of the displacement (12) can be expressed by the dielectric permeability  $\varepsilon(T)$ . For the sake of definitiveness, we will also discuss the case of perovskites with a phase transition from the cubic phase to the tetragonal phase. Then the matrices  $A$ ,  $V$  and  $S$  in (12) will be given by (1.9), and the matrix  $Q$  according to (1.24b) with  $T > T_0$  will be equal to zero. Let us introduce [while integrating over  $\vec{k}$  in (12)] the new variable  $x = |\vec{k}| \sqrt{\varepsilon/\lambda}$ , so that the integral becomes

$$\langle u_\alpha u_\beta \rangle_c = - \frac{T}{24\pi^3} \frac{\delta_{\alpha\beta}}{\rho} \left( \frac{\lambda}{\varepsilon} \right)^{\frac{1}{2}} \int_0^\infty dx \int d\vec{n} \, Sp \left[ \chi (1+x^2 \phi)_t^{-1} \phi_t^{-1} \chi^+ \right] \quad (14)$$

Here  $\rho = M/v_c$  equals density,  $d\vec{n}$  represents integration over the vector angles  $\vec{n}$  and the matrices  $\chi$  and  $\phi$  depend only on the angles  $\vec{n}$ :

$$\chi = (a_l g^l + a_t g^t + a_a g^a)^{-1} (v_t g^t + v_a g^a) ;$$

$$\phi = s_t g^t + s_a g^a - (v_t g^t + v_a g^a) \chi ;$$

$$g_{\alpha\beta}^t = \delta_{\alpha\beta} - g_{\alpha\beta}^l = \delta_{\alpha\beta} - n_\alpha n_\beta ; \quad g_{\alpha\beta}^a = \sum_{\sigma=1}^3 e_\sigma^\alpha e_\sigma^\beta (\vec{n} \vec{e}_\sigma)^2 \quad (15)$$

where  $\vec{e}_\sigma$  are the unit vectors of the principal axes of the crystal, and  $a_i$ ,  $v_i$ ,  $s_i$  are constants introduced in (1.9).

Thus, the anomalous portion of the displacement above the transition is increased with an approach to  $T_0$ , which decreases in abso-

lute value in inverse proportion to the root of the dielectric permeability.

In the tetragonal phase, the permeability along the tetragonal axis  $x$ ,  $\epsilon_{xx} = \epsilon_{\parallel}$ , is (as a rule) less than the transverse permeability  $\epsilon_{yy} = \epsilon_{zz} = \epsilon_{\perp}$ . Therefore, the conversion of the variables in the integral according to  $\vec{k}$  can be done more suitably with the aid of  $\epsilon_{\perp} : x = |\vec{k}| \sqrt{\frac{\epsilon_{\perp}}{\lambda}}$ , after which (12) is written in the form

$$\langle u_{\alpha} u_{\beta} \rangle_c = \frac{T}{8\pi^3 \rho} \left( \frac{\lambda}{\epsilon_{\perp}} \right)^{\frac{1}{2}} \int_0^{\infty} dx \int d\vec{n} \left| \left[ \frac{1}{\hat{a} - (x\hat{v} + i\hat{q}P\sqrt{\frac{\lambda}{\pi\rho}})(\delta^{\perp} + \delta^{\parallel} \frac{\epsilon_{\perp}}{\epsilon_{\parallel}} + x^2 \hat{s})^{-1} (x\hat{v} - i\hat{q}P\sqrt{\frac{\lambda}{\pi\rho}}) - \frac{1}{\hat{a} - \hat{v}(\hat{s})_t^{-1} \hat{v}} \right]_{\alpha\beta} \right|. \quad (16)$$

Here  $P$  is the polarization, and the matrices entered into the system, related to the axes of the crystal according to [1], have the form

$$\hat{v} = \begin{pmatrix} v_t + v_a n_1^2 & 0 & 0 \\ 0 & v_t + v_a n_2^2 & 0 \\ 0 & 0 & v_t + v_a n_3^2 \end{pmatrix}$$

$$\hat{q} = \begin{pmatrix} (q_{11} - \frac{q_{44}}{4})n_1 & 0 & 0 \\ q_{12}n_2 & \frac{q_{44}}{4}n_1 & 0 \\ q_{12}n_3 & 0 & \frac{q_{44}}{4}n_1 \end{pmatrix}; \quad (17)$$

$$\delta^{\perp} + \delta^{\parallel} \frac{\epsilon_{\perp}}{\epsilon_{\parallel}} + x^2 \hat{s} = \begin{pmatrix} \frac{\epsilon_{\perp}}{\epsilon_{\parallel}} + x^2(s_t + s_a n_1^2) & 0 & 0 \\ 0 & 1 + x^2(s_t + s_a n_2^2) & 0 \\ 0 & 0 & 1 + x^2(s_t + s_a n_3^2) \end{pmatrix}.$$

Here,  $\hat{a} = a_l g^l + a_t g^t + a_a g^a$  is the matrix of the elastic coefficients,  $q_{ik}$  are the striction constants, and the components  $(\dots)_t^{-1}$  are located according to the rule (13).

Therefore, below  $T_0$  there is anisotropy of the vibrations  $\langle u_x^2 \rangle_c \neq \langle u_y^2 \rangle_c = \langle u_z^2 \rangle_c$ . The temperature dependence of the displacement is determined by the temperature curve of the permeability  $\varepsilon$  and the polarization  $P$ . If the transition is close to the transition of the second type so that below  $T_0$  the relationship for  $\varepsilon$  /39

and  $P \sim \frac{1}{T_c - T}$ ,  $P \sim \sqrt{T_c - T}$  is fulfilled to a satisfactory degree, the anomaly of the displacement is likewise proportional to  $|T_c - T|^{\frac{1}{2}}$  above the transition.

If the elastic, striction, and dielectric properties of the crystal are known, then expressions (12), (14), and (16) contain four unknown constants, which we can represent, e.g., by  $\frac{\lambda}{s_t}$ ,  $\frac{v_t^2}{s_t}$ ,  $\frac{s_a}{s_t}$ ,  $\frac{v_a}{v_t}$ . In the low-frequency spectrum of the crystal, in addition to these constants, we have two more: the actual value  $\lambda$  and the mass constant  $\mu$  [1]. Reduction of the number of constants is related to the fact that the use above of discarding in the sum for frequencies of  $\omega_n$  combined with  $n \neq 0$  correspond to the classical description of motion, when in the equilibrium function of the distribution the multipliers with a kinetic energy are separated from the terms with potential energy. As a result, in the average values of the compound, the mass characteristics contained in the kinetic energy drop out.

In the general case, the integrals (12), (14) and (16) must be taken numerically. For illustration and explanation of the physical picture, let us consider as in [1] the hypothetical case of an isotropic crystal in which  $a_a = v_a = s_a = 0$ . As mentioned in [1], such an estimate is definitely satisfactory and quantitative for the cubic crystals under consideration. Calculation in this case is more likely to lead to a system of coordinates where one of the axes is directed along  $\vec{k}$  and the other is perpendicular to  $\vec{k}$  and the tetragonal axis. If in (16) we carry out integration over  $x$ , for the anomaly of the cross section of the thermal displacements we will obtain

$$\langle u_x^2 + u_y^2 + u_z^2 \rangle_c = \frac{T}{4\pi\rho} \left( \frac{\lambda}{\varepsilon_{\perp} W} \right)^{\frac{1}{2}} \int_0^1 dz \left[ \frac{P^2 \varepsilon_{\perp}}{\pi\rho} \left( \frac{\xi^2 + \eta^2}{\sqrt{R_1}} + \frac{q_{44}^2 n_{\perp}^2}{16a_t^2 \sqrt{R_{\perp}}} \right) - \frac{v_t^2}{W a_t^2} \left( \sqrt{R_1} + \sqrt{R_{\perp}} \right) \right]. \quad (18)$$

Here

$$z = n_1; \quad n_{\perp}^2 = 1 - z^2; \quad \xi = \frac{n_1}{a_t} \left( \frac{q_{44}}{4} + q_a n_{\perp}^2 \right);$$

$$\eta = \frac{n_{\perp}}{a_{\perp}}(q_{12} + q_a n_1^2); \quad q_a = q_{11} - q_{12} - \frac{q_{44}}{2}; \quad W = s_t - \frac{v_t^2}{a_t}; \quad (19)$$

$$R_{\perp} = n_1^2 + n_{\perp}^2 \frac{\epsilon_{\perp}}{\epsilon_{\parallel}} - \frac{P^2 \epsilon_{\perp}}{\pi \rho} (a_t \xi^2 + a_{\perp} \eta^2); \quad R_{\parallel} = 1 - \frac{P^2 \epsilon_{\perp}}{\pi \rho} \frac{q_{44}^2 n_1^2}{16 a_t}.$$

Equation (18) consists of two parts: the striction, proportional to  $P^2$  and the "completely critical" latter term. The contribution of these terms to the anomaly of the displacement is different. In transition to the ferroelectric phase, each of the values  $\epsilon_{\parallel}$  and  $\epsilon_{\perp}$  is less than the value  $\epsilon$  of the high-temperature phase; therefore, the rigidity for the critical vibrations below the transition increases by jumps, which in the absence of terms with  $P$  would lead to an abrupt reduction of the amplitudes of the vibrations and an increase in the Mössbauer emission. With a further decrease in temperature,  $\epsilon$  and the vibrational amplitudes continue to form so that the temperature dependence of the Debye-Waller factor which is observed would have the form shown in Figure 1a. However, the term with  $P^2$  describes the increase of the vibrational amplitude as a function of the appearance of a piezoelectric relationship between the acoustic and critical branches, which reduces the elastic moduli. Therefore, the resulting sign of the jump in the Debye-Waller factor at the transition point depends on the relationship of the values  $v_t^2/s_t$  and  $P^2 \epsilon_{\perp}$  at  $T = T_0$ . The further changes in temperature are also determined by the concurrence of these two terms. It is possible to show that the picture which has been described with contributions having different signs is also retained in considering the anisotropic terms  $s_a$ ,  $v_a$ , and  $a_a$ .

The experimental results, particularly in [3], clearly show that the conventional situation is that shown in Figure 1b, when the jump in the factor  $f$  at the transition point is negative, i.e., the strictional jump is larger. In addition, there is a fall in the amplitudes and an increase in  $f$ , i.e., the second term in (18) increases with a drop in temperature which is more rapid than the first.

It would be interesting to have more experimental material in order to get an idea of the degree of generality of such a theory. /41  
At the present time, however, we can only point out, for example, that in the case of  $\text{BaTiO}_3$ , the increase with the decline in  $T$  of the second term (18) relative to the first is natural, since in this substance below  $T_0$  the values  $P$  and  $\epsilon_{\perp}$  change to a very small extent, while  $\epsilon_{\parallel}$  decreases rapidly [10], so that the ratio  $\epsilon_{\perp}/\epsilon_{\parallel}$ , involved in  $R_{\perp}$ , increases rapidly.

Let us also introduce the expression for the anisotropy of the vibrations below  $T_0$  in the case  $s_a = v_a = a_a = 0$ . As designated in

(19), we have

$$\langle u_y^2 \rangle_c - \langle u_x^2 \rangle_c = \frac{T}{8\pi\rho} \left( \frac{\lambda}{W\epsilon_{\perp}} \int_0^1 dz \left[ \frac{P^2 \epsilon_{\perp}}{\pi \rho} \left( \frac{(\xi n_{\perp} - \eta n_{\perp})^2 - 2(\xi n_{\perp} + \eta n_{\perp})^2}{\sqrt{R_1}} \right. \right. \right. \\ \left. \left. \left. + \frac{q_{44}^2 n_{\perp}^2}{16 a_t^2 \sqrt{R_1}} \right) + \frac{v_t^2}{W a_t^2} \left( (2 - 3 n_{\perp}^2) \sqrt{R_1} - \sqrt{R_{\perp}} \right) \right] \right). \quad (20)$$

Determination of the sign of (20) requires more careful estimates. We can point out, however, that as  $\epsilon_{\perp} / \epsilon_{\parallel}$  increases,  $R_1$  increases, so that at values of  $v_t^2 / s_t$  which are not too small, (20) is positive. Since in  $\text{BaTiO}_3$ , we have assumed that the Ti ion is the one most strongly bonded with the critical vibration, then the result mentioned in [2] regarding the sign of the anisotropy of the vibrations of Ti agrees with that expected from (20). However, the degree of anisotropy of about 50%, given in [2], appears to be too high. Estimates with the aid of (20) give a value for the anisotropy on the order of 0.01-0.1.

#### 4. ORDER-DISORDER TRANSITIONS

For order-disorder transitions [10], ions or group of ions have several symmetrical positions of equilibrium in the cell, which have statistically equal populations above transition, while below transition there is a spontaneous asymmetry of the population, as in the familiar Ising model. The full potential at which the ion moves can be strongly anharmonic, so that the picture of the transition differs from the case of transitions of displacement type. We will show that in this case the probability of the Mössbauer effect in the vicinity of the transition may show anomalies.

Previously, in the transition from (1) to (2) and (3), we made use of the fact that the line width  $\Gamma$  is much less than the characteristic frequencies of the motion of the ions, which in the case of displacement type transition were optical frequencies. In the given case, the characteristic time is the relaxation time  $\tau$  of the distribution of the ions in the cells to equilibrium. The Mössbauer effect will be sensitive to transition only in the case when the irradiation time  $1/\Gamma$  is greater than or on the order of  $\tau$ . In ferroelectrics, the order of the value of  $\tau$  can be estimated experimentally from data on the dispersion of the dielectric permeability [11, 12]. The values  $\tau$  and  $1/\Gamma$  change within wide limits and can be commensurate with one another. /42

For the sake of simplicity, we will initially disregard the quadrupole and magnetic fission and limit ourselves to the case of small  $q$ , when the exponents in (1) can be divided according to degrees of  $qu$ :

$$W = \frac{\sigma_0 \Gamma}{2\pi} \int_{-\infty}^{\infty} dt e^{i(\omega - \omega_0)t - \Gamma|t|} \left[ 1 + q_\alpha q_\beta (\langle u_\alpha(0) u_\beta(t) \rangle - \langle u_\alpha(0) u_\beta(0) \rangle) \right]. \quad (21)$$

For a qualitative description of the phenomena related to the transition, we will assume that the correlation function of the coordinates falls with  $t$  according to a simple exponential law with a relaxation time  $\tau$  [12]:

$$\begin{aligned} \langle (u_\alpha(0) - \bar{u}_\alpha)(u_\beta(t) - \bar{u}_\beta) \rangle &= \langle u_\alpha(0) u_\beta(t) \rangle - \bar{u}_\alpha \bar{u}_\beta = \\ &= (\langle u_\alpha(0) u_\beta(0) \rangle - \bar{u}_\alpha \bar{u}_\beta) e^{-t/\tau}. \end{aligned} \quad (22)$$

Then (21) gives:

$$W = \frac{\sigma_0}{\pi} \left[ \frac{\Gamma}{(\omega - \omega_0)^2 + \Gamma^2} + q_\alpha q_\beta \left( \langle u_\alpha(0) u_\beta(0) \rangle - \bar{u}_\alpha \bar{u}_\beta \right) \left( \frac{\Gamma + 1/\tau}{(\omega - \omega_0)^2 + (\Gamma + 1/\tau)^2} - \frac{\Gamma}{(\omega - \omega_0)^2 + \Gamma^2} \right) \right]. \quad (23)$$

In the case of large relaxation times  $\Gamma\tau \gg 1$ , the terms in parentheses in (23) are shortened. In this case the atom cannot jump from one potential hole to another during the radiation time and the result is naturally that it is not sensitive to the transition point. In the case  $\Gamma\tau \sim 1$ , the dependence of the probability upon the frequency takes the form of the superposition of two lines of equal width. With approach to the transition point, the area of the narrow line (as we can see later on) is reduced somewhat, while the area of the wide one increases. Finally, in the case  $\Gamma\tau \ll 1$ , the first term in parentheses in the frequency range  $|\omega - \omega_0| \ll 1/\tau$  is much smaller than the second. We then see (as in the case of the displacement-type transitions) that the probability of absorption is expressed by the correlation function of the ions and shows a particular feature at the transition point. /43

For explaining the nature of this peculiarity, let us use the model which was used previously in [12,13] and begin by evaluating the case of a nonferroelectric transition. The Hamiltonian of this model has the form

$$H = \sum_{\bar{r}} \frac{m \dot{x}_{\bar{r}}^2}{2} + \sum_{\bar{r}} u(x_{\bar{r}}) - \frac{1}{2} \sum_{\bar{r} \neq \bar{r}'} V(\bar{r} - \bar{r}') x_{\bar{r}} x_{\bar{r}'}, \quad (24)$$

For the sake of simplicity, let us limit our consideration to uni-dimensional motion:  $x_{\bar{r}}$  is the coordinate of the ion relative to the

center of the cell,  $u(x) = u(-x)$  is the anharmonic potential of the ion in the cell; the potential  $V(\vec{r})$  has spherical symmetry and a large but finite radius of motion  $r_0$ . A phase transition of the second type is included in the appearance with  $T = T_c$  of an average displacement relative to the center. The transition takes place at high temperatures, so that the motion of the ions can be considered classical.

Using the method given in [13,14], the desired value of the correlation function in the first approximation for  $1/r_0^3$  can be written in the form

$$\langle (x-\bar{x})^2 \rangle = \frac{\int_{\vec{r}} \Pi d\vec{x}_{\vec{r}} (x_{\vec{r}} - \bar{x})^2 \exp \left[ -\beta u(x_{\vec{r}}) + \beta V_0 \bar{x} x_{\vec{r}} + \frac{\beta}{2} \sum_{\vec{r}, \vec{r}'} \tilde{V}(\vec{r} - \vec{r}') (x_{\vec{r}} - \bar{x})(x_{\vec{r}'} - \bar{x}) \right]}{\int_{\vec{r}} \Pi d\vec{x}_{\vec{r}} \exp \left[ -\beta u(x_{\vec{r}}) + \beta V_0 \bar{x} x_{\vec{r}} + \frac{\beta}{2} \sum_{\vec{r}, \vec{r}'} \tilde{V}(\vec{r} - \vec{r}') (x_{\vec{r}} - \bar{x})(x_{\vec{r}'} - \bar{x}) \right]} \quad (25)$$

Here  $V_0 = \sum_{\vec{r}} V(\vec{r})$ , and the effective interaction  $\tilde{V}$  analogous to the Debye potential [14] is considered as the correlation of the particles in the first approximation:

$$\tilde{V}(\vec{r}) = \sum_{\vec{k}} \frac{V_{\vec{k}}}{1 - \beta V_{\vec{k}} \langle (x-\bar{x})^2 \rangle_0} e^{i\vec{k}\vec{r}} ; \quad V_{\vec{k}} = \sum_{\vec{r}} V(\vec{r}) e^{-i\vec{k}\vec{r}} \quad (26) \quad /44$$

The indication  $\langle \dots \rangle_0$  means that the averaging takes place at  $\tilde{V} = 0$ . In the transition region  $\beta \tilde{V}(\vec{r})$  there is a small value on the order of  $r_0^{-3}$  [13]. If we expand (25) over  $\beta \tilde{V}$ , we obtain

$$\langle (x-\bar{x})^2 \rangle = \overline{x^2(T)} - x_0^2 + \frac{1}{2} \left[ \langle (x-x_0)^4 \rangle_0 - (\overline{x^2} - x_0^2)^2 \right] \sum_{\vec{k}} \frac{\beta V_{\vec{k}}}{1 - \beta V_{\vec{k}} (\overline{x^2} - x_0^2)}, \quad (27)$$

where  $x_0 = \bar{x}(T)$ ,  $\overline{x^2}(T) = \langle x^2 \rangle_0$

In this approximation the transition temperature is  $T_c = V \overline{x^2}(T_c)$ . Therefore, in the region of small  $k$  and  $|T - T_c|$  the denominator of the Green's function in (27) has the form

$$1 - \beta V_{\vec{k}} (\overline{x^2} - x_0^2) = \frac{k^2 r_0^2}{6} + \alpha \frac{T - T_c}{T_c} + \frac{x_0^2}{x^2}; \quad (28)$$

$$r_0^2 = \frac{1}{V_0} \sum_{\vec{r}} r^2 V(\vec{r}); \quad \alpha = 1 + T_c \frac{d}{dT} \ln \overline{x^2}(T) \Big|_{T=T_c}$$



Hence, the sum over  $\vec{k}$  in (27) has the same form as in (12), (14) and (16), and the anomaly of the quadratic displacement is proportional to  $|T-T_c|^{1/2}$ . The expression in brackets in (27) is positive, so that the probability of the Mössbauer effect always has a minimum at the transition point, in accordance with the reduced rigidity for long-wave fluctuations in the vicinity of  $T_c$ . In the case under consideration, with large  $r_0$ , the second term in (27) below the transition is proportional to  $T-T_c$  and greater than the third term as far as  $r_0^3 v_c$  is concerned. Therefore, in the region of applicability of the approximation used [13],  $T_c \gg |T-T_c| > \frac{v_c^2}{r_0^6} T_c$  is /45 the probability of the Mössbauer absorption below  $T_c$  and is much greater than that at  $|T-T_c|$  above the transition, and increases linearly with  $T_c-T$ .

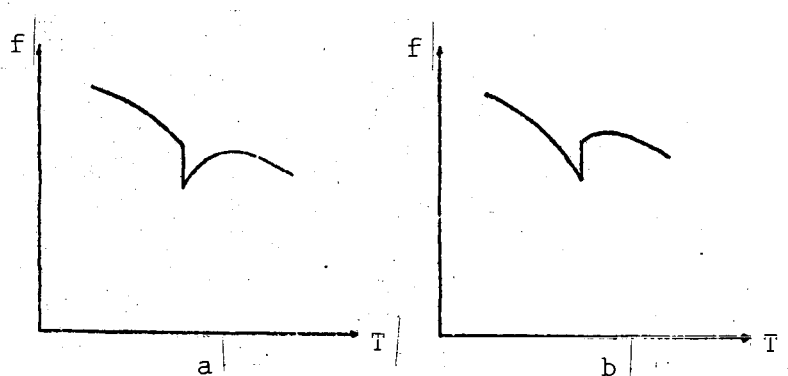
In ferroelectrics, order-disorder transitions are characteristic of uniaxial crystals. In these cases, there is a significant influence of long-range dipole-dipole interaction [13,12]. Thus, at  $T > T_c$  the correlation function in the range of small  $\vec{k}$  is given by the expression [13]:

$$\langle x_{\vec{k}} x_{-\vec{k}} \rangle = \frac{\overline{x^2}}{\frac{k^2 r_0^2}{6} + \lambda \frac{\overline{x^2}}{T_c} \left( \frac{1}{\epsilon} + n_x^2 \right)} ; \quad \lambda = \frac{4\pi e_{eff}^2}{v_c} ; \quad n_x = \frac{k}{k} . \quad (29)$$

Here  $\epsilon$  is the dielectric permeability, proportional to  $1/(T-T_c)$ ,  $e_{eff}$  is the effective charge of the ions and it is assumed that it is much greater than the inverse dimensions of the sample  $1/L$ . This formula differs from the analogous expression in (28) as far as the supplementary term  $n_x^2$  in the denominator is concerned, giving correlation effects at small  $k$ . As a result, the anomalous portion of the quadratic displacements in the vicinity of  $T_c$ , instead of being radical, will have a weaker characteristic  $\sim |T-T_c| \ln |T-T_c|$ :

$$f^2 = f^2(T_c) \left[ 1 + q^2 \frac{\overline{x^4} - (\overline{x^2})^2}{\overline{x^2}} \frac{v_c}{r_0^3} \frac{3\sqrt{6}}{8\pi} \left( \frac{\lambda \overline{x^2}}{T_c} \right)^{1/2} \frac{\ln \epsilon}{\epsilon} \right]. \quad (30)$$

Note that in the case of the order-disorder transitions, when the anharmonicity is not small, a special portion  $f$  does not contain the small factor  $T/\epsilon_{at}$ , which is found for displacement type transitions (12). Therefore the peculiarity, generally speaking, must be noticeable. This can partially compensate for the weaker character of the peculiarity (30); however, comparison with experiments requires more detailed investigation.



## 5. CONCLUSIONS

From what has been stated above, it is clear that studies of the Mössbauer effect in the phase transition region are of considerable interest. In the case of displacement type transitions, for which it is possible to formulate a quantitative description, these measurements make it possible to measure the microscopic constants. In the case of order-disorder transitions, the Mössbauer measurements can give qualitative information regarding the relaxation times and the transition parameters.

It is also very interesting to consider the Mössbauer measurements in the field of nonferroelectric structural transitions of the first type in crystals. The dielectric properties do not show any anomalies in this case. Therefore it is always clear whether or not the transition is close to a transition of the second type (as in transitions of displacement type in ferroelectrics) or whether the phases above and below the transition are very different, and the anomalies (corresponding to the second type transitions) are absent.

It is clear that the characteristic minimum for the probability of a Mössbauer emission is related to the correlation effects and the reduction in the rigidity of the system for long-wave correlations. However, in the case of "normal" transition of the first type, this probability must (generally speaking) have as its transition point only a jump and a break in the temperature dependence; However, there must not be any decline in the approach to the transition. Therefore, relatively simple Mössbauer measurements can give reliable information regarding the nature of the transition.

## REFERENCES

1. Vaks, V. G.: Phase Transitions of Displacement Type in Ferroelectrics, Part I of "O fazovykh perekhodakh v segnetoelektrikakh" (Phase Transitions in Ferroelectrics), Institute of Atomic Energy im. I. V. Kurchatov (Moscow), 1967, 46 p.
2. Danner, H. R., B. C. Fraser and R. Pepinsky, cited in: Iona, F. and D. Shirane: Segnetoelektricheskiye kristally (Ferroelectric Crystals), Mir (Moscow), 1965, p. 212.

3. Sklyarevskiy, V. V, I. I. Lukashevich, V. P. Romanov, N. I. Filippov, Yu. N. Venevtsev, and A. S. Viskov: Zhur. Eksptl i Teoret. Fiz., Pis'ma v Redaktsiyu, Vol. 3, p. 212, 1966.
4. Bhide, V. G. and M. S. Mhetani: Phys. Rev., Vol. 139, p. 1983, 1965.
5. Muzikář, C., V. Janovec, and Dvořák: Phys. Stat. Sol., Vol. 3, p. K9, 1963.
6. Kagan, Yu. M. (ed.): Effekt Mössbauera (The Mössbauer Effect), Inostrannaya Literatura (Moscow), 1962.
7. Lamb, W. E.: Phys. Rev., Vol. 55, p. 190, 1939; Van Hove, L.: Phys. Rev., Vol. 95, p. 249, 1954.
8. Abrikosov, A. A., L. P. Gor'kov, and I. E. Dzyaloshinskiy: Metody kvantovoy teorii polya v statisticheskoy fizike (Methods of Quantum Field Theory in Statistical Physics), Fizmatgiz (Moscow), 1962.
9. Cochran, W.: Adv. Phys., Vol. 9, p. 387, 1960; Vol. 10, p. 401, 1961.
10. Iona, F. and D. Shirane: Segnetoelektricheskiye kristally (Ferroelectric Crystals), Mir (Moscow), 1965.
11. Hill, R. M. and S. K. Tchiki: Phys. Rev., Vol. 128, p. 1140, 1962; Vol. 132, p. 1603, 1963.
12. Vaks, V. G., V. M. Galitskiy, and A. I. Larkin: Zhurn. Eksptl. i Teoret. Fiz., Vol. 51, p. 1592, 1966.
13. Vaks, V. G., A. I. Larkin, and S. I. Pikin: Zhurn. Eksptl. i Teoret. Fiz., Vol. 51, p. 361, 1966.
14. Landau, L. D. and E. M. Lifshits: Statisticheskaya fizika (Statistical Physics), Nauka (Moscow), 1964, Sections 75, 76.

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